

SUMMARY REPORT No. 1  
**CHARACTERISTICS AND STABILIZATION OF  
THE BAINITE REACTION**

In Cooperation With  
The Office of Naval Research, U. S. Navy  
NONR-763(00) Project NR-031-471  
**MARCH 1954**

THIS REPORT HAS BEEN DELIMITED  
AND CLEARED FOR PUBLIC RELEASE  
UNDER DOD DIRECTIVE 5200.20 AND  
NO RESTRICTIONS ARE IMPOSED UPON  
ITS USE AND DISCLOSURE.

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE;  
DISTRIBUTION UNLIMITED.

An Investigation Of  
THE KINETICS OF THE BAINITE REACTION IN ALLOY STEELS

Summary Report No. 1

CHARACTERISTICS AND STABILIZATION OF THE BAINITE REACTION

By

R. F. Hehemann  
and  
A. R. Troiano

Conducted By  
METALS RESEARCH LABORATORY  
DEPARTMENT OF METALLURGICAL ENGINEERING  
CASE INSTITUTE OF TECHNOLOGY

In Cooperation With  
OFFICE OF NAVAL RESEARCH, U. S. NAVY

Contract Nonr - 763(00)

Project NR-031-471

Cleveland, Ohio  
February, 1954

METALS RESEARCH LABORATORY  
DEPARTMENT OF METALLURGICAL ENGINEERING  
CASE INSTITUTE OF TECHNOLOGY

Summary Report No. 1

CHARACTERISTICS AND STABILIZATION OF THE BAINITE REACTION

Written By:

---

R. F. Hehemann

---

A. R. Troiano  
Task Order Director



DISTRIBUTION LIST FOR

Summary Report

No. 1

Copy No. \_\_\_\_\_

Contract Nonr - 763(00)

February, 1954

Project NR-031-471

Copy No.

1-2

Chief of Naval Research  
Department of the Navy  
Washington 25, D. C.  
Attn: Code 423

3

Director  
Office of Naval Research  
Branch Office  
150 Causeway Street  
Boston, Massachusetts

4

Director  
Office of Naval Research  
Branch Office  
346 Broadway  
New York 13, New York

5-6

Director  
Office of Naval Research  
Branch Office  
844 North Rush Street  
Chicago 11, Illinois

7

Director  
Office of Naval Research  
Branch Office  
1000 Geary Street  
San Francisco 9, California

8

Director  
Office of Naval Research  
Branch Office  
1030 E. Green Street  
Pasadena 1, California

Copy No.

9-10

Assistant Naval Attache for Research  
Office of Naval Research  
Branch Office  
Navy 100  
c/o Fleet Post Office  
New York, New York

11-16

Director  
Naval Research Laboratory  
Washington 25, D. C.  
Attn: Technical Information Officer

17

Office of Technical Service  
Department of Commerce  
Washington 25, D. C.

18

Director, Naval Research Laboratory  
Washington 25, D. C.  
Attn: Code 3500, Metallurgy Div.  
Code 2020, Technical Library

19-21

Bureau of Aeronautics  
Department of the Navy  
Washington 25, D. C.  
Attn: N. E. Promisel, AE-41  
Technical Library, TD-41

22

Commanding Officer  
Naval Air Material Center  
Naval Base Station  
Philadelphia, Pennsylvania  
Attn: Aeronautical Materials Lab.

23-25

Bureau of Ordnance  
Department of the Navy  
Washington 25, D. C.  
Attn: Rex  
Tech. Library, Ad3

26

Superintendent, Naval Gun Factory  
Washington 25, D. C.  
Attn: Metallurgical Lab., DE 713

27

Commanding Officer  
U. S. Naval Ordnance Laboratory  
White Oaks, Maryland

Copy No.

28	Commanding Officer U. S. Naval Ordnance Test Station Inyokern, California
29-31	Bureau of Ships Department of the Navy Washington 25, D. C. Attn: Code 343 Code 337L, Tech. Library
32	U. S. Naval Engineering Experiment Station Annapolis, Maryland Attn: Metals Laboratory
33	Director, Materials Laboratory Building 291 New York Naval Shipyard Brooklyn 1, New York Attn: Code 907
34	Bureau of Yards & Docks Department of the Navy Washington 25, D. C. Attn: Research & Standards Division
35	Post Graduate School U. S. Naval Academy Monterey, California Attn: Dept. of Metallurgy
36	Chief of Staff, U. S. Army The Pentagon Washington 25, D. C. Attn: Director of Research & Development
37-39	Office of the Chief of Ordnance Research & Development Service Department of the Army Washington 25, D. C. Attn: ORDTB - E. L. Hollady
40	Commanding Officer Watertown Arsenal Watertown, Massachusetts Attn: Laboratory Division

Copy No.

- 41                    Commanding Officer  
                     Frankford Arsenal  
                     Frankford, Pennsylvania  
                     Attn: Laboratory Division
- 42                    Office of the Chief of Engineers  
                     Department of the Army  
                     Washington 25, D. C.  
                     Attn: Research and Development Branch
- 43                    U. S. Air Forces  
                     Research and Development Division  
                     The Pentagon  
                     Washington 25, D. C.
- 44                    Wright Air Development Center  
                     Wright-Patterson Air Force Base  
                     Dayton, Ohio  
                     Attn: Materials Laboratory  
                                 Flight Research Laboratory  
                                 (J. B. Johnson)
- 45                    Commanding Officer  
                     Office of Ordnance Research  
                     Duke University  
                     Durham, North Carolina  
                     Attn: Metallurgy Division
- 46                    Atomic Energy Commission  
                     Division of Research  
                     Metallurgical Branch  
                     Washington 25, D. C.
- 47                    National Bureau of Standards  
                     Washington 25, D. C.  
                     Attn: Physical Metallurgy Division
- 48                    National Advisory Committee for  
                                 Aeronautics  
                     1724 F Street, N. W.  
                     Washington 25, D. C.
- 49                    Research and Development Board  
                     The Pentagon  
                     Washington 25, D. C.  
                     Attn: N. C. Fick

Copy No.

50	Argonne National Laboratory P. O. Box 5207 Chicago 80, Illinois Attn: Dr. Hoylande D. Young
51	U. S. Atomic Energy Commission 1901 Constitution Avenue, N.W. Washington 25, D. C. Attn: B. M. Fry
52	Brookhaven National Laboratory Information and Publication Div. Documents Section Upton, New York Attn: Miss Mary E. Waisman
53	Carbide & Carbon Chemicals Division Plant Records Department Central Files (K-25) P. O. Box P Oak Ridge, Tennessee
54	Carbide & Carbon Chemicals Division Central Reports & Information Office (Y-12) P. O. Box P Oak Ridge, Tennessee
55	General Electric Company Technical Services Division Technical Information Group P. O. Box 100 Richland, Washington Attn: Miss M. G. Freidank
56	Iowa State College P. O. Box 14A, Station A Ames, Iowa Attn: Dr. F. H. Spedding
57	Knolls Atomic Power Laboratory P. O. Box 1072 Schenectady, New York Attn: Document Librarian

Copy No.

58	Los Alamos Scientific Laboratory P. O. Box 1663 Los Alamos, New Mexico Attn: Document Custodian
59	Mound Laboratory U. S. Atomic Energy Commission P. O. Box 32 Miamisburg, Ohio Attn: Dr. M. M. Haring
60	U. S. Atomic Energy Commission New York Operations Office P. O. Box 30, Ansonia Station New York 23, New York Attn: Div. of Tech. Information & Declassification Service
61	Oak Ridge National Laboratory P. O. Box P Oak Ridge, Tennessee Attn: Central Files
62	Sandia Corporation Sandia Base Classified Document Division Albuquerque, New Mexico Attn: Mr. Dale M. Evans
63	U. S. Atomic Energy Commission Library Branch, Technical Information Service, ORE P. O. Box E Oak Ridge, Tennessee
64	University of California Radiation Laboratory Information Division Room 128, Building 50 Berkeley, California Attn: Dr. R. K. Wakerling

Copy No.

- |    |  |
|----|--|
| 65 | Westinghouse Electric Corporation<br>Atomic Power Division<br>P. O. Box 1468<br>Pittsburgh 30, Pennsylvania<br>Attn: Librarian |
| 66 | Professor G. L. Kehl<br>Dept. of Metallurgical & Mining<br>Engineering<br>Columbia University<br>New York, New York            |
| 67 | Professor M. Cohen<br>Department of Metallurgy<br>Massachusetts Institute of Technology<br>Cambridge 39, Massachusetts         |
| 68 | Professor C. Wells<br>Metals Research Laboratory<br>Carnegie Institute of Technology<br>Pittsburgh, Pennsylvania               |
| 69 | Professor J. E. Dorn<br>Department of Engineering<br>University of California<br>Berkeley, California                          |
| 70 | Professor E. P. Klier<br>Department of Chemical Engineering<br>University of Maryland<br>College Park, Maryland                |

## CHARACTERISTICS AND STABILIZATION OF THE BAINITE REACTION

### ABSTRACT

Kinetically, the bainite reaction in steels is characterized by a relatively rapid transformation which begins after an induction period, proceeds isothermally, and then comes to a halt without necessarily resulting in complete decomposition of the austenite. This remaining untransformed austenite may remain dormant for extended lengths of time. A characteristic temperature exists above which austenite will not transform into bainite. Below this temperature the amount of austenite transformed to bainite increases as the transformation temperature is lowered. A lower temperature limit also exists below which it may be possible to obtain complete decomposition of the austenite to bainite.

If austenite is reacted in the bainite range at a temperature where the transformation does not result in complete decomposition, then additional transformation may be obtained by subsequent reaction at a lower temperature. Reaction at the lower temperature is retarded by the prior treatment and a smaller amount of austenite is decomposed by the bainite reaction. This stabilization phenomenon is most readily recognized by the requirement for a new induction period at the lower temperature.

Interpretation of these results is based on a mechanism involving a limitation in the nucleation and growth of bainite plates.



# CHARACTERISTICS AND STABILIZATION OF THE BAINITE REACTION

## INTRODUCTION

Although the past twenty years have seen rapid advances in our understanding of the reactions occurring in the pearlite and the martensite transformations in steel, the mechanism of the bainite reaction has remained obscure. In fact, even the kinetic features which serve to define this transformation were not fully recognized prior to isothermal studies on medium alloy compositions in which the pearlite and bainite reactions are separated with respect to time and temperature. These investigations have shown that, although the reaction curve for the formation of bainite is similar to that for a nucleation and growth transformation, other kinetic features are more in keeping with the martensitic mode of transformation. Part I of this paper presents a correlated review of the literature on the bainite reaction.

It is now well known that the austenite-martensite transformation may be stabilized by slow cooling through the martensite range or by holding either above or below the  $M_s$  temperature. This stabilization process, which involves no compositional changes in the untransformed austenite, is characterized by a lowering of  $M_s$  and an increase in the amount of austenite at any arbitrary reference temperature. Although the existence of a similar phenomenon in the transformation of austenite to bainite would have considerable

theoretical and practical significance, the bainite reaction has not been studied from this point of view. The present investigation fulfills this need through a study of the effect of partial reaction at one temperature upon the kinetics of reaction at another (lower) temperature in the bainite range. The results of this study are discussed in Part II of the paper.

## PART I

### REVIEW OF THE LITERATURE

#### GENERAL KINETIC FEATURES

The kinetics of the bainite reaction have been studied by metallographic, dilatometric, magnetic, and electrical resistance methods (1-21, 44).<sup>\*</sup> Transformation at constant temperature is characterized by the reaction curve illustrated in Fig. 1. Austenite decomposition begins slowly, accelerates for a short period of time, and then decelerates to an extremely low rate after long transformation times. The general form of this reaction curve is similar to that for typical nucleation and growth processes such as the eutectoid decomposition. When reaction curves similar to those in Fig. 1 are combined in the familiar T-T-T diagram, the curve designating the beginning of transformation has a "C" shape. In these respects,

-----  
<sup>\*</sup> Numbers in parenthesis refer to the bibliography at the end of the paper.

the transformation of austenite to bainite is similar to that of austenite to pearlite; however, significant differences between the two reaction types prevents extension of this analogy. Specifically, complete decomposition of austenite can be attained at all temperatures in the pearlite range, whereas, Fig. 1 demonstrates that partial decomposition to bainite is achieved quite rapidly whereupon this transformation stops (3-18).<sup>\*</sup> Fig. 2 demonstrates that the amount of austenite transformed by this rapid reaction becomes greater as the decomposition temperature is lowered. When no other reaction (pearlite, etc.) overlaps the bainite range, the austenite not transformed to bainite is extremely persistent and remains untransformed for exceptionally long periods of time.

A well defined temperature exists above which austenite will not transform to bainite, (24). This temperature, which has been designated  $B_s$  is determined by the composition of the austenite. As revealed in Fig. 2, the amount of austenite transformed to bainite increases from zero percent at  $B_s$  to one-hundred percent at some lower temperature (6-8, 11). The progress of the extent of decomposition as a function of reaction temperature exhibits a striking similarity to the corresponding relationship (M-T curve) for the

-----  
<sup>\*</sup> This property is so characteristic of the austenite-bainite transformation that it appears desirable to speak of a rapid bainite reaction and bear in mind the fact that this rapid reaction does not necessarily transform all of the austenite.

martensite transformation.\* It should be recalled, however, that for a given analysis the  $B_s$  and  $M_s$  temperatures are separated widely with respect to temperature. Furthermore, for a given temperature below  $M_s$ , the amount of martensite characteristic of this temperature appears during the time required to cool from  $M_s$  to the reaction temperature. That is, the martensite transformation cannot be suppressed. In contrast to the behavior of the martensite reaction, high cooling rates prevent the formation of bainite. Consequently, the amount of bainite characteristic of a particular reaction temperature requires the time span of the isothermal reaction for its formation.

The behavior of the austenite remaining after the rapid reaction is not well understood at the present time. In view of the relatively high temperatures at which the reaction remains incomplete (700-1000°F), eventual disappearance of the austenite must be anticipated; however, the reaction sequence may become extremely complex (6, 7, 11). The pearlite reaction is effective in consuming this austenite for those compositions in which the two reactions overlap (11, 17, 44). For more highly alloyed steels, in which overlapping does not appear to occur, it has been suggested (5) that the rapid reaction does not completely stop but continues at a greatly reduced rate. Lineal analysis studies (65) of the bainite reaction in a medium

-----  
\* In view of the parallelism between this kinetic feature of the bainite and martensite transformations, the highest temperature at which the rapid reaction transforms all of the austenite will be designated  $B_f$  and the curve itself will be designated the B-T curve.

alloy, hypoeutectoid steel, however, have shown no increase in the amount of transformation product throughout the time interval from 3 to 280 hours. An alternate suggestion (18) is that a secondary reaction, which is initiated well after the end of the rapid reaction, completes the decomposition process.\*

#### INFLUENCE OF THERMAL AND MECHANICAL HISTORY

Reaction kinetics in the bainite range are radically altered by the prior thermal and mechanical treatment of the specimen. The effect of partial decomposition at one temperature on transformation kinetics at another temperature is of special interest in connection with the nucleation process controlling the phase transformation. Reaction at the first temperature may influence that at the second temperature by changing the composition of the austenite or by modification of the nucleation of the reaction product at the second temperature. Obviously, small amounts of transformation cannot create major changes in austenite chemistry. Under this condition, any influence of prior transformation on the progress of reaction at another temperature must result from modifications of the nucleation process.

The time required for the formation of 1% bainite (induction

- 
- \* This secondary reaction was not considered to be a low temperature extension of the conventional pearlite reaction. Hultgren (74) has suggested recently that there can also be a low temperature form of pearlite which is kinetically separated from the high temperature form.

period) in hypoeutectoid steels is appreciably shortened by a brief interruption in the proeutectoid ferrite range during quenching (22, 23, 25). On the other hand, holding an hypereutectoid steel in the proeutectoid carbide range markedly delays the bainite transformation (23, 9). It has been suggested (22, 23) that these observations confirm the hypothesis (58, 62) that bainite is nucleated by ferrite rather than by cementite.

The influence of large amounts of proeutectoid constituents on the bainite reaction is complicated by the changes in austenite chemistry which accompany these reactions. The carbon enrichment of austenite resulting from the formation of proeutectoid ferrite should retard subsequent transformation in the bainite range. This has been confirmed experimentally (75). The prior formation of pearlite plus proeutectoid carbide has been shown to accelerate the bainite reaction in high speed steel (15). Since it has been demonstrated (76) that the bainite reaction is essentially unaffected by the prior formation of pearlite alone, it appears likely that the acceleration associated with the simultaneous precipitation of pearlite and carbide is due to the impoverishment of carbon in the austenite resulting from the proeutectoid reaction.

Critical examination of scattered data obtained by several investigators (9, 10, 23) appears to indicate that reaction at a low temperature in the bainite range is retarded when preceded by

isothermal treatment at a higher temperature in this range. It further appears that retardation increases and the total amount of decomposition decreases as the holding time at the higher temperature is prolonged.

Transformation at a low temperature in the bainite range (9, 23, 26, 27) or at temperatures below  $M_s$  (16, 26, 30, 31) accelerates the bainite reaction at higher temperatures. Under appropriate conditions, the induction period at the higher temperature can be completely eliminated by the low temperature reaction (26).

The isothermal bainite transformation is relatively insensitive to the prior austenite grain size (4, 69); however, recent studies (70) indicate that austenitizing temperature may exert a role beyond that attributable to changes in grain size or to homogenization. It has been shown that the bainite reaction is accelerated when high austenitizing temperatures are employed and that this phenomenon is essentially reversible. If cooling from a high austenitizing temperature is interrupted at a lower temperature in the austenitic range, then the rate of the bainite reaction returns close to that obtained by a single austenitizing treatment at the lower temperature.

The effect of externally applied stresses on the bainite transformation has not received widespread attention; however, it has been demonstrated that such stresses accelerate the reaction (33-36). Furthermore, although the data are fragmentary, there are

indications that the total amount of bainite may also be increased.

#### EFFECTS OF COMPOSITION

Recent surveys (37-39) of the available literature indicate that the addition of carbon and all of the common alloying elements will lower  $B_s$  and reduce the rate of reaction. The most powerful effect is associated with the addition of carbon. Substitutional alloying elements are less effective than carbon by approximately one order of magnitude and stand in the order: manganese, chromium, nickel, and molybdenum. It should be noted that the behavior of the individual elements parallels their influence on the  $M_s$  temperature.

The relationship between composition and the  $B_f$  temperature has generally not been recognized in the literature. Studies of Krupp type carburizing steels (40) and of three percent chromium steels (6) indicate that this temperature is relatively insensitive to carbon content. At least for a wide variety of medium alloy steels (6, 40, 41) it is also insensitive to alloy content (nickel, chromium, and molybdenum in various combinations) and falls within a relatively narrow temperature range around  $600^\circ - 700^\circ\text{F.}$ \* The compression of the temperature range of incomplete austenite decomposition in the higher carbon and alloyed steels results from the fact that an increase in the

- - - - -  
\* The fact that many of the lower alloyed steels do not exhibit this characteristic is believed to be due to the intervention of other types of transformation which may occur in the upper bainite temperature range (11, 17).



amount of these elements depresses  $B_s$  without lowering  $B_f$ .

No relationship has been observed between the  $M_s$  and  $B_f$  temperatures. The  $B_f$  temperature, therefore, may be either above or below  $M_s$  depending upon the analysis of the steel. In those compositions in which  $M_s$  is above  $B_f$ , it is not possible to produce a fully bainitic structure by any of the conventional thermal treatments. The full significance of this condition frequently has not been appreciated in commercial practice and undoubtedly has helped to further the concept that the mechanical properties of bainitic structures are inferior to those of tempered martensite.

In compositions for which  $M_s$  is below  $B_f$ , it is, of course, possible to obtain fully bainitic structures. An increase of carbon content expands the temperature range between  $M_s$  and  $B_f$  because of its potent effect in lowering  $M_s$ . The higher carbon steels thus lend themselves more readily to heat treating cycles designed around fully bainitic structures.

#### MICROSTRUCTURAL AND CRYSTALLOGRAPHIC OBSERVATIONS

Numerous authors have surveyed the literature on the structure and morphology of bainite (39, 44, 55, 56). Bainite is an aggregate of ferrite and carbide, but there is no certainty that the structure initially forms in this fashion.

Although bainitic structures assume a variety of forms, all are

more or less acicular. As in the case of martensitic structures (29) the appearance of bainite is dictated primarily by the temperature of formation rather than the composition of the austenite. At the top of the range, the structure resembles an acicular ferrite with carbide particles dispersed throughout the ferrite. This structure has been termed the "X" constituent (57). The average carbide particle size in the ferrite becomes smaller as the transformation temperature is lowered until, at reaction temperatures near  $M_s$ , the structure assumes the appearance of tempered martensite. The morphology of the structure changes gradually with reaction temperature so that no sharp discontinuities are observed over any narrow temperature range.

In compositions for which both pearlite and bainite form at the same temperature, the size of the carbide particles is smaller in pearlite than in bainite. Hardness and metallographic observations as well as electron microscope studies (46-48, 56) have shown that the carbide in bainite is less finely distributed than that in a martensitic structure tempered at the same temperature. Electron microscope studies (71) demonstrate that the carbide phase is present as small, parallel platelets preferentially oriented with respect to the needle axis.

The crystallography of the products resulting from austenite decomposition in the bainite range has been studied by several investigators (28, 58). In eutectoid steels, bainite formed at 840 and

750°F displayed the Nishiyama lattice relationship between austenite and ferrite; whereas, that formed at 680°F exhibited the Kurdjumov and Sachs relationship. No data have been published on the lattice relationship between austenite and the carbide phase of bainitic structures.

The orientation habit of bainite in a 0.92% plain carbon steel was found to vary continuously with transformation temperature. Basically, the habit plane does not delineate any low indice plane of the austenite. The habit plane was approximately octahedral at 840°F and varied along a  $\langle 134 \rangle$  austenite zone as the transformation temperature was lowered.

#### NATURE OF THE CARBIDE PHASE

The carbide resulting from austenite decomposition in the bainite range (at least above approximately 600°F) is invariably cementite regardless of the alloy content of the steel (3, 6-8, 10, 42-47). The alloy content of this cementite follows that of the austenite (42-47); i.e., there is little or no partition of alloying elements associated with this transformation. Continued treatment at the transformation temperature or tempering at a higher temperature will tend to concentrate the alloying elements in either the ferrite or the carbide phase.

The carbide in the bainite formed at temperatures below approximately 600°F (relatively high carbon steels) is different from the

cementite formed at higher temperatures. Magnetic measurements reveal no cementite curie point (3, 73) and dilatometric measurements (21) produce total expansions which are larger than those predicted on the basis of a ferrite plus cementite structure. It has been suggested (3, 21) that these results reflect the formation of ferrite supersaturated with respect to carbon; however, an alternate possibility (73) is that the carbide precipitates in some transition state. A recent electron diffraction study (48), which revealed epsilon iron carbide in bainitic structures formed at 500 to 550°F, favors the latter interpretation.

#### COMPOSITION OF THE UNTRANSFORMED AUSTENITE

It is well known that partial transformation in the bainite range lowers  $M_s$  of the untransformed austenite and increases the amount of austenite retained at room temperature (6, 7, 9, 10, 12-15, 17, 28). This has been attributed by some investigators to enrichment of the austenite in carbon as a result of the transformation (45). It has been observed, however, that  $M_s$  can be lowered by holding in the bainite range for times less than that required for the formation of visible amounts of transformation product (29, 32) and that high-purity, binary iron-chromium (6) and iron-manganese (10) alloys also retain greater amounts of austenite at room temperature after partial transformation at higher temperatures. No carbon enrichment has been detected in high carbon steels (28, 26, 7, 52) in spite of the fact that

the amount of retained austenite is increased and  $M_s$  is lowered by partial reaction. Lattice parameter measurements of retained austenite in steels containing 0.3 to 0.4% carbon have indicated carbon enrichment (8, 14, 49-51); however, one wonders if this must not be attributed to the formation of proeutectoid ferrite.\* Lowering of  $M_s$  and/or increased retention of austenite by partial reaction, therefore, does not constitute sufficient evidence for carbon enrichment. A true stabilization process (53) may also be active in the bainite range. On this basis, it appears that no gross changes occur in either the carbon or alloy contents of the austenite remaining after the bainite transformation.

#### REACTION MECHANISM

Any hypothesis for the mechanism of the bainite reaction must be consistent with the many reliable experimental observations most of which are encompassed in the following:

- (a) The transformation product consists of an aggregate of ferrite and cementite.
- (b) Transformation occurs by a thermal process involving an induction period. At sufficiently high cooling rates, the reaction can be completely suppressed.
- (c) A temperature ( $B_s$ ) exists above which bainite does

-----  
\* Hultgren (44) suggests that a probainitic ferrite may also occur in many hypoeutectoid steels.

not form. This temperature is sensitive to the composition of the austenite.

- (d) Isothermal reaction at temperatures near  $B_s$  stops before all of the austenite has been transformed.
- (e) The amount of austenite consumed by the isothermal reaction increases as the reaction temperature is lowered. Complete decomposition can be achieved at all temperatures below  $B_f$ .

All the mechanisms which have been proposed for the transformation of austenite to bainite may be classified into two basically different categories. One (2, 8, 56, 59, 60, 63, 64) requires that bainite initially forms as supersaturated ferrite by a lattice shearing process. Carbide particles subsequently precipitate from this ferrite. In effect, this point of view implies that bainite is delayed martensite. According to the other proposal (28, 44), bainite forms directly from austenite as an aggregate of ferrite and cementite. Proponents of both mechanisms agree that the transformation is nucleated by ferrite rather than by cementite.

According to the supersaturated ferrite mechanism,  $B_s$  represents that temperature at which stress free ferrite and austenite of identical composition are in equilibrium (59, 60). Thermodynamic arguments qualitatively predict the correct variation of  $B_s$  with carbon content;

however, experimental  $B_s$  temperatures are lower than the calculated ones. It has been suggested (60) that carbon is adsorbed on bainite nuclei which would produce the lower  $B_s$  temperature. Since martensite also forms as supersaturated ferrite, one must account for the difference between the  $B_s$  and  $M_s$  temperatures. This difference has been attributed to a strain energy effect (59).

In order to account for the induction period of the bainite reaction, it has been proposed (8, 56) that low carbon regions must be born at the transformation temperature as a result of statistical fluctuations in composition. These low carbon regions effectively raise  $M_s$  locally above the transformation temperature as a result of which these regions shear into supersaturated ferrite. A more or less similar explanation (60) suggests that embryos\* (austenite regions with low carbon concentration) retained from the austenitizing treatment are initially subcritical in size. The induction period represents the time required for these embryos to grow to the critical size. Upon attaining the critical size, a bainite plate would form in a fraction of a second.

Proponents of the supersaturated ferrite mechanism suggest that this state enjoys only a transient existence. Shortly after the creation of a bainite plate, supersaturation is lost by precipitation of carbide

\* The same embryo which produces the first bainite plate would have produced the first martensite plate had cooling been continued below  $M_s$ .

within the ferrite and by diffusion of carbon into the surrounding austenite. This carbon enrichment presumably lowers  $B_s$  below the reaction temperature so that austenite is no longer unstable with respect to supersaturated ferrite. Transformation would therefore stop before all of the austenite had been consumed. Gross enrichment of the untransformed austenite has not been detected, however, in any case where the transformation product was unquestionably bainite. Although a localized carbon concentration gradient surrounding bainite plates could stop their growth, this hypothesis does not explain why new plates do not nucleate at some distance from the existing ones (24). It must be concluded that even though a localized enrichment may occur, this does not explain why all of the austenite does not succumb to the bainite reaction at temperatures near  $B_s$ .

The incomplete nature of the bainite reaction finds a more plausible explanation in the concept of nucleation by embryos retained from the austenitizing treatment. The number of embryos of a given size is restricted to a distribution created at the austenitizing temperature. At the transformation temperature, only those embryos which are larger than some critical size will be promoted to nuclei (60, 79). Once these have been activated, nucleation, and consequently transformation, would stop. The observation that the amount of bainite becomes greater as the reaction temperature is lowered is consistent with the effect of temperature on the size of stable nuclei.



The mechanism based on supersaturated ferrite requires that the mode of development of a bainite plate be identical with that of a martensite plate. Surface relief effects have been observed in the transformation of austenite to bainite (27), which were similar to those involved in the formation of martensite; however, each plate developed in a slow, continuous manner. In view of the high diffusion rate of carbon in ferrite, as well as in austenite at the temperatures involved, slow growth of supersaturated ferrite becomes impossible since the carbon should flow from the ferrite into the austenite. In the absence of rapid propagation, the concept of the formation of supersaturated ferrite becomes untenable.\*

In considering bainite to form as an aggregate, two different modes of transformation suggest themselves. The transformation may involve either the separate formation of ferrite and cementite (28, 44) from austenite, or the precipitation of cementite within the ferritic phase (60). The latter will be given further consideration in a subsequent section of this paper.

The mechanism based on the separate precipitation of ferrite and cementite from austenite was developed from observations of the structure and composition of bainite. Here, the transformation is considered to be nucleated by a special form of ferrite (termed

-----  
\* This does not rule out the formation of ferrite with a special metastable equilibrium carbon content (44).

para ferrite) which inherits its alloy content from austenite while its carbon content corresponds to a special, metastable equilibrium value dictated by the transformation temperature. Formation of this ferrite enriches the surrounding austenite in carbon so that cementite (with the alloy content of the austenite) forms in juxtaposition to the ferrite. The ferrite then continues its growth around the cementite particle. Recently, electron micrographs (61) have been advanced to support the structural features of this mechanism. The kinetic features of the bainite reaction have not been rationalized in terms of this hypothesis.

## PART II

### EXPERIMENTAL STUDY OF REACTION KINETICS

#### MATERIALS AND PROCEDURE

Two triple alloy steels were chosen for this investigation. Their compositions were:

<u>Designation</u>	<u>Composition-Weight Percent</u>						<u>Aust. Temp. °F</u>
	<u>C</u>	<u>Si</u>	<u>Mn</u>	<u>Ni</u>	<u>Cr</u>	<u>Mo</u>	
4340	0.38	0.28	0.74	1.79	0.81	0.26	1550
K	0.31	0.30	0.76	3.07	1.22	0.49	1650

These steels were chosen because the pearlite reaction did not interfere with the bainite reaction.

Steel K was received in the cast condition and forged from 2" square bars to 1/2" x 1-3/4" plates. The 4340 was received as

1-1/4" hot rolled rounds. Both steels were homogenized in vacuum for one week at 2300°F in order to minimize segregation.

A quenching dilatometer similar to that described by Flinn, Cook and Fellows (5) was employed for the kinetic measurements. Dimensional changes were detected by a differential transformer and recorded on a Leeds and Northrup Speedomax recorder. The dilatometer was mounted on a vertical post so that it could be transferred to any one of three furnaces: a nitrogen atmosphere austenitizing furnace and two salt bath furnaces for isothermal transformation. Dilatometer specimens were 1/32" x 1/4" x 1-1/2" with a gauge length of 1.4". All specimens were nickel plated in order to minimize decarburization during austenitizing. The austenitizing conditions consisted of 10 minutes at the temperatures given above. Austenitizing temperatures were controlled to  $\pm 10^{\circ}\text{F}$  and transformation temperatures to  $\pm 3^{\circ}\text{F}$ . The precision of the dimensional measurements was estimated to be  $\pm 5 \times 10^{-5}$  inches per inch.

## RESULTS AND DISCUSSION

### Isothermal Transformation

The characteristics of the isothermal bainite reaction for these steels will be described first in order to erect a framework from which it will be possible to evaluate the influence of partial reaction at one temperature in the bainite range on the kinetics of reaction at

another temperature. Isothermal expansion curves for the bainite reaction in 4340 are illustrated in Fig. 3. These curves are typical of the behavior of both 4340 and the K steels. As a first approximation, dilation curves are a direct measure of the progress of the reaction since the amount of expansion is approximately proportional to the amount of decomposition product.

Fig. 3 demonstrates that the general shape of the reaction curve remains unchanged throughout the temperature interval above  $M_s$ . The isothermal reaction is characterized by a short induction period during which expansion is negligible, followed by a time period during which transformation proceeds rapidly. Reaction soon stops, but all of the austenite does not transform. This characteristic of the bainite reaction is most evident in the reduced overall expansion resulting from reaction at the higher temperatures.

A semi-quantitative picture of the way in which the extent of decomposition depends on transformation temperature (B-T curve) can be obtained from the total isothermal expansion (6, 7). This is presented as a function of reaction temperature in Fig. 4 for 4340 and Fig. 5 for the K Steel. The  $B_s$  temperature is determined by extrapolation of this curve to zero percent expansion. Thus, it becomes apparent that bainite forms only below this characteristic temperature and that the amount of bainite becomes greater as the temperature is lowered. Metallographic examination indicated that  $B_f$  was 730°F for

4340 and 610°F for the K steel. The total dilation continued to increase as the reaction temperature was lowered below  $B_f$ . Some increase in total dilation must be anticipated here because of the difference in the coefficients of thermal expansion of the austenitic and the ferritic phases; however, the slope of the curve below  $B_f$  is too great to be accounted for by this means. The reason for this anomalous behavior is not clear.

The shape of the reaction curve at temperatures below  $M_s$  (curve for 575°F in Fig. 3) is different from that observed above  $M_s$ . This does not reflect a fundamental change in the characteristics of the bainite reaction but rather is the result of the integrated contributions of the martensite and the bainite transformations. The initial expansion starting at 4 to 5 seconds results from the athermal martensite transformation; whereas, the isothermal martensite reaction (68) permits transformation to continue even after the specimen has attained the bath temperature (10 seconds). The inflection point at approximately 35 seconds thus signifies the start of the normal bainite reaction. Aside from the marked acceleration in reaction rate, the prior formation of martensite has not altered the basic kinetic features of the bainite transformation.

Time-temperature-transformation diagrams for the bainite range of the 4340 and K steels were constructed from the dilatometric data and are presented in Figs. 6 and 7. The time for the start and end of

the rapid reaction was arbitrarily chosen as that at which the expansion attained 1% and 99% respectively of the total isothermal expansion. Comparison of Figs. 6 and 7 affords an excellent illustration of the lack of correlation between  $M_s$  and  $B_f$  (see earlier discussion). Both steels have approximately the same  $M_s$ ; however, there is a temperature difference of approximately 100°F between their  $B_f$  temperatures. In fact,  $B_f$  was slightly below  $M_s$  in the K steel. This is an example of a composition in which it is not possible to produce a fully bainitic structure by any known thermal treatment.

At temperatures near the top of the bainite range in 4340 the pearlite reaction is initiated if the isothermal treatment is continued well beyond the end of the bainite reaction. As illustrated in Fig. 6, the pearlite reaction is accelerated by the prior formation of bainite in the same fashion as the bainite reaction is accelerated by the prior formation of martensite at reaction temperatures below  $M_s$ . The pearlite reaction in the K steel was not initiated within five days at any temperature in the bainite range.

#### Stepped Reactions

Conventional nucleation and growth concepts suggest that a reaction initiated at one temperature in a metastable region should continue upon quenching to a different temperature. A new induction period should not be required at the second temperature. In view of the

significance of such thermal history effects in the formulation of an adequate hypothesis for the reaction mechanism, a detailed knowledge of these kinetic features becomes virtually mandatory. Therefore, specimens were reacted at a high temperature in the bainite range\* for a predetermined period of time and then quenched to a lower temperature. Fig. 8 compares two curves for reaction at 800°F. Curve A illustrates the progress of the normal reaction (direct quench) at this temperature. In curve B, transformation at 800°F was preceded by reaction for 45 minutes at 935°F. The 935°F treatment resulted in 24% bainite, the maximum amount attainable at this temperature. Reaction at  $T_h$  (935°F) has increased the induction period from 28 to 64 seconds and has appreciably reduced the rate of transformation throughout the progress of the test. Although the reaction rate at  $T_r$  has been lowered, the fundamental kinetic feature of a rapid, incomplete reaction has been preserved.

In addition to the retardation of reaction prior transformation at the higher temperature has stabilized part of the austenite against decomposition at  $T_r$ . This is clearly revealed in the influence of prior transformation on the total dilation at  $T_r$ . Obviously, transformation at  $T_h$  must reduce the total expansion at  $T_r$ ; however, even when the expansion corresponding to the amount of decomposition at

-----  
\* In the following, the first reaction temperature will be designated  $T_h$  and the second  $T_r$ .

$T_h$  is added to that occurring at  $T_r$ , the total dilation is less than that obtained by direct reaction. This summation is accomplished in Fig. 8 by a displacement of curve B (prior treatment at 935°F) with respect to curve A (direct reaction) by an amount equal to the expansion obtained by reaction at 935°F. It is significant to note that, even after this correction has been made, the prior transformation has prevented the total expansion from attaining that resulting from direct reaction. This difference is a measure of the amount of austenite stabilized by the prior treatment. The semi-quantitative observations of stabilization obtained with the dilatometer have been confirmed by lineal analysis and will be discussed more fully in a later section.

The principal factors controlling the retardation process are the holding time, the holding temperature ( $T_h$ ), the amount of transformation, and the reaction temperature  $T_r$ . Although all these are not independent variables, insufficient data are available to permit a complete separation of their individual contributions. It is possible, nevertheless, to define the general features of the retardation phenomenon and to indicate some of the inter-relationships between the contributing factors. For this purpose, the induction period at  $T_r$  will be employed as a criterion of the retardation produced by partial reaction at  $T_h$ .



### Effect of Reaction Temperature ( $T_R$ )

The dependence of the induction period of 4340 on reaction temperature ( $T_R$ ) is illustrated in Fig. 9. This figure compares the induction period observed at  $T_R$  after prior transformation for 45 minutes at  $T_h$  levels of 950, 935 and 900°F with that resulting from direct reaction at  $T_R$ . At reaction temperatures near the holding temperature, the induction period at  $T_R$  has been lengthened appreciably by the prior transformation at  $T_h$ , i.e., reaction at  $T_R$  has been retarded. The amount of retardation becomes less as the difference between  $T_h$  and  $T_R$  is increased. In fact, there is an apparent reversal of the retardation effect at reaction temperatures below approximately 700°F.

The K steel responded to prior treatment at  $T_h = 800^\circ\text{F}$  in a manner analogous to that of 4340, see Fig. 10. A holding period of two hours at 800°F has retarded transformation at all lower temperatures. Again, the amount of retardation decreased as the reaction temperature was lowered.

It is significant to note that, in each of the cases examined, an induction period has been required at the second reaction temperature ( $T_R$ ). The induction period at  $T_R$  suggests that the reaction initiated at  $T_h$  has not continued at  $T_R$ . This concept receives added weight from an examination of the microstructure produced at  $T_R$ . If the transformation product formed at  $T_h$  had continued its growth at

$T_r^*$ , then, after the double treatment, the microstructure should consist of platelets of the high temperature product more or less completely surrounded by low temperature bainite. The structure of 4340 obtained by treating 1 hour at 930°F followed by 3 minutes at 700°F is reproduced in Fig. 11. Although the low temperature product (dark platelets) does appear to nucleate in the vicinity of the high temperature bainite (light platelets), its principal direction of growth does not, in general, coincide with that of the high temperature plate. None of the low temperature product is visible around a majority of the high temperature plates. It thus appears that normal growth of the high temperature product does not take place at the lower temperature. New plates of low temperature bainite are formed both within the austenite and at the austenite/prior bainite interface.

#### Effect of Time at the Holding Temperature ( $T_h$ )

In the experiments described above, the time at  $T_h$  (45 minutes) has been equal to or greater than that required to permit transformation to stop. The results are therefore clouded by the fact that the amount of bainite formed at  $T_h$  becomes greater as this temperature is lowered. In an attempt to separate the effects of holding time, holding temperature, and amount of bainite, specimens of 4340 were

-----  
\* At a rate dictated by  $T_r$ .

reacted for various times at  $T_h$  levels of 965, 935, and 900°F and then quenched to  $T_r$  levels of 800 or 700°F. The induction period at  $T_r = 800^\circ\text{F}$  and  $700^\circ\text{F}$  is presented as a function of holding time at  $T_h$  in Figs. 12 and 13 respectively.

The holding time at  $T_h$  exerts a strong effect on the behavior at  $T_r$ . Short holding times at  $T_h$  reduce the induction period at  $T_r$  slightly, however, in no case has it been eliminated. Therefore, the reaction initiated at  $T_h$  does not continue at  $T_r$  even when transformation is still in progress at the instant of quenching to  $T_r$ . This is substantiated by the structure produced in 4340 by reaction for 2 minutes at 940°F followed by 50 seconds at 660°F. This structure is illustrated in Fig. 14. It may be noted again that the reaction product initiated at  $T_h$  has not continued its growth at  $T_r$ .

Since a short period of time at  $T_h$  reduces the induction period at  $T_r$  to something less than its normal value, it would at first appear that the reaction at  $T_r$  has been accelerated by the prior treatment. This however is more apparent than real. On the basis of total reaction time, the mere fact that a new induction period is required at  $T_r$  indicates that the reaction, in reality, has been retarded by the prior treatment. This retardation of reaction at  $T_r$  becomes more pronounced as the holding time at  $T_h$  is prolonged. The induction period at the second temperature ( $T_r$ ) exceeds its normal value when reaction at the holding temperature ( $T_h$ ) has proceeded to an appreciable

extent. The arrows in Figs. 12 and 13 designate the time at which the rapid reaction at  $T_h$  attains 90% of its total. It may be noted that only the last 10%\* of the reaction at  $T_h$  results in significant retardation at lower temperatures. Indeed, the phenomenon producing retardation continues even in the absence of detectable transformation, i.e., even after transformation at  $T_h$  has stopped. Fig. 15 demonstrates that the K steel responds to variation of the holding time in much the same manner as 4340. The major retardation is again associated with holding periods near the end of reaction at  $T_h$ .

By analogy with the stabilization process associated with the martensite transformation (54) it might be anticipated that the amount of retardation would approach a limiting value as the holding time at  $T_h$  is extended. The maximum amount of retardation should increase as  $T_h$  is lowered. Figs. 12 and 13 indicate that this is true for 4340 although the limiting value of the induction period is not much greater after treatment at  $T_h = 900^\circ\text{F}$  than it is at  $T_h = 935^\circ\text{F}$ . In the K steel, the induction period at  $700^\circ\text{F}$  is still increasing after prior treatment for five days at  $800^\circ\text{F}$ . Evidently, a time longer than five days is required to achieve the limiting state in this steel.

#### Relative Influence of $T_h$ and Percent Bainite

It is clearly demonstrated in Figs. 12 and 13 that the maximum

-----  
\* 10% of the transformable amount and not 10% reaction product.

amount of retardation at a given reaction temperature ( $T_r$ ) increases as the holding temperature ( $T_h$ ) is lowered. Since the amount of bainite at the end of transformation also increases as  $T_h$  is lowered, the relationship between the effect of holding temperature and percent bainite on retardation is not apparent. On the other hand, the retardation process cannot be attributed solely to the amount of transformation at  $T_h$ . Thus, 18% bainite formed by holding for 45 minutes at 950°F lengthens the induction period at 800°F from 28 to 50 seconds. The same amount of bainite formed by holding for 2 minutes at 900°F shortens the induction period at 800°F from 28 to 18 seconds. Since major retardations are associated only with the last few percent of transformation at  $T_h$  regardless of the actual level of transformation, it appears that there may be a relation between the processes which produce the incomplete nature of the bainite reaction and the retardation phenomenon.

In addition to a general retardation of the reaction rate, Figs. 9 and 10 reveal that prior transformation at  $T_h$  also causes a lowering of the  $M_s$  temperature. The similarity between the effects of holding in the bainite and in the martensite (54) ranges on  $M_s$  is striking, and as in the latter case, depression of  $M_s$  by prior transformation signifies the operation of a stabilization process.

### Stabilization of the Austenite-Bainite Reaction

It has been indicated that partial reaction at  $T_h$  does not eliminate the incomplete nature of the bainite reaction but actually decreases the amount of bainite attainable under certain circumstances. This stabilization of the bainite transformation has been studied by the lineal analysis technique (67). The effect of 45 minutes at several holding temperatures on the total extent of reaction after subsequent treatment at 800°F is illustrated in Fig. 16. Ninety-seven percent decomposition is obtained by direct reaction at this temperature. As an illustration of the interpretation of this figure consider reaction at  $T_h = 925^\circ\text{F}$ . It is observed that 31 percent austenite is transformed to bainite at  $T_h$  and that an additional 52 percent transforms during subsequent reaction at 800°F. Prior transformation at 925°F has thus reduced the total transformation from 97 to 83%. In other words, 14% austenite has been stabilized. The cross hatched region in Fig. 16 thus represents the amount of austenite stabilized against reaction at 800°F by the prior treatment at  $T_h$ .

The amount of stabilized austenite increases as  $T_h$  is lowered below 985°F, passes through a maximum, and decreases again as the holding temperature approaches the reaction temperature. This characteristic of stabilization of the bainite reaction is, therefore, very similar to the corresponding characteristic of the martensite reaction (54). In the latter transformation, the maximum amount of

stabilization occurs at that temperature at which all of the austenite not transformed at  $T_h$  is stabilized against reaction at  $T_r$ . This is not the case in the stabilization process associated with the transformation of austenite to bainite.

Transformation at one temperature will effect the course of the B-T curve at lower temperatures. The effect of transformation for 45 minutes at 935°F on the shape of the B-T curve is depicted in Fig. 17. The stabilization treatment has reduced the total amount of decomposition for all reaction temperatures between 935 and 750°F; however, the  $B_f$  temperature was unaffected by the stabilization treatment. Stabilization at holding temperatures of 900°F and 965°F was also without effect upon the  $B_f$  temperature. In fact, no thermal treatment capable of displacing this temperature has been found.\* This insensitivity of  $B_f$  to the prior treatment represents a distinct difference between the characteristics of stabilization of the bainite and the martensite reactions. Once again another point of departure in the behavior of bainite and martensite is observed.

The amount of austenite stabilized at  $T_r$  will also depend upon the holding time at  $T_h$ . The upper part of Fig. 18 illustrates the effect of holding time at 935°F on the total amount of transformation after reaction at 800°F. There is very little change in the total

-----  
\* A treatment capable of raising this temperature would afford considerable advantage in commercial heat treating practice.

amount of transformation until the time of interruption at 935°F exceeds 500 to 600 seconds. The reaction curve at 935°F, presented in the lower part of Fig. 18, demonstrates that the bainite reaction has proceeded to within 90% of the total during this time so that it is again the last few percent of the bainite reaction at  $T_h$  which is most effective in producing stabilization at  $T_r$ . Although the amount of stabilized austenite appears to reach a plateau value after approximately 2500 seconds, initiation of the pearlite reaction reestablishes the stabilization process.

#### Practical Significance of the Retardation Phenomenon

The retardation of the bainite reaction resulting from partial decomposition at high temperatures in the bainite range suggests that it may be possible to increase appreciably the hardenability of these and similar steels with only a slight sacrifice in maximum hardness. Troiano (77) has conducted end quench tests employing prior retardation treatments on a steel intermediate in analysis between that of the 4340 and K steels of the present investigation. Hardenability test bars were quenched in salt for 20 minutes at 935° and 950°F respectively prior to the normal end quench test. Fig. 19 illustrates the effect of the prior retardation treatment on the hardenability characteristics. Transformation at the holding temperature (935°F or 950°F) has reduced slightly the hardness at



the water quenched end of the bar. The sample treated at 935°F exhibited a lower hardness than the one treated at 950°F because of the larger amount of bainite formed at the lower temperature. Although the maximum hardness has been reduced, the position along the bar at which the hardness deviates from this value has been increased considerably. In fact, the specimen held at 935°F essentially retained its maximum hardness along the entire length of the end quenched bar. It is clear that an appreciable improvement in hardenability has resulted from each of these interrupted quenching treatments.

The difference in behavior between the tests conducted at 950 and 935°F is in qualitative agreement with the retardation picture developed previously. Fig. 12 demonstrates that, for constant holding time, the retardation becomes greater as the holding temperature is lowered. This is revealed in Fig. 19 by the fact that the specimen treated at 935°F did not decrease appreciably in hardness along the entire length of the bar, whereas, the specimen held at 950°F did exhibit some loss in hardness at positions beyond about 1-1/2 inches from the water quenched end of the bar.

This retardation phenomenon may have even more far reaching significance in explaining the hardenability response of medium carbon, alloy steels. In general, appropriate alloy combinations produce a significant reduction in the rate of the reactions which

occur in the pearlite range, whereas, their effect on the rate of the bainite reaction is considerably less. In spite of the short induction period for the isothermal bainite reaction, such steels frequently exhibit excellent hardenability in the end quench test. Apparently some stabilization of the bainite transformation occurs during continuous cooling through the bainite range in order to provide the excellent hardenability response of these compositions.

### RATIONALIZATION OF REACTION KINETICS

#### The Isothermal Reaction

The major kinetic features of the bainite reaction have not been adequately explained by any of the existing hypotheses for the reaction mechanism. It now seems certain that a nucleation and limited growth process is involved. Unlike other nucleation and growth processes, the amount of austenite consumed by the bainite reaction is a function of the transformation temperature. This signifies that both nucleation and growth of the transformation product stops prior to the disappearance of all austenite.

Morphological studies indicate that bainite forms as plates (probably coherent with austenite) in which the lateral growth is much more rapid and extensive than the growth in thickness. The growth of a bainite plate may be limited by loss of coherency resulting from excessive matrix and precipitate strains or by

impingement with grain boundaries, inclusions, or other plates. This limitation on the growth of bainite plates signifies that each nucleus transforms only a small fraction of the available austenite before its growth is terminated.

Two conditions may be visualized which could interrupt the nucleation process: a) compositional changes in the austenite may lower the free energy change associated with the transformation so that a quasi-equilibrium state is attained, or b) nuclei may appear only at certain high energy regions in the austenite. Once these have been consumed, transformation would virtually cease in the absence of growth.

The currently available experimental evidence points to the fact that no gross compositional changes accompany the transformation. Therefore, the former supposition must be discarded. Although a formal treatment is not yet possible, the concept involving nucleation from a limited number of high energy regions appears to offer the greatest promise of providing a means for rationalizing the kinetic characteristics of the bainite reaction.

Although the concept of homogeneous nucleation requires that nuclei form at random throughout a parent phase, a variety of theoretical and experimental evidence indicates that they actually appear at certain preferred locations (72). Such nucleation has been termed heterogeneous (78). These nucleation sites may be

grain boundaries, inclusions, embryos retained from the austenitizing treatment, or other crystal imperfections. Statistical fluctuations which occur at the austenitizing temperature create two types of regions capable of functioning as embryos for the bainite reaction. They may be low carbon regions with the austenitic structure or they may be regions with a ferritic structure. In the former case, the low carbon, austenitic region may actually become ferritic on quenching to the reaction temperature. For the present purpose, the embryos will be viewed as regions with the ferritic structure and a carbon and alloy content which corresponds to the average composition of the austenite. The number of regions of a specific size is restricted to a distribution inherited from the austenitizing treatment. These embryos, which are retained at the transformation temperature, are initially subcritical in size and consequently will not become larger until there is an appropriate modification in their composition. This implies that the activation of embryos solely by configurational fluctuations does not occur at a detectable rate.

The activation of a particular embryo is accomplished by a process which lowers the critical size to that of the embryo. As illustrated schematically in Fig. 20, the critical size of a ferritic region becomes smaller (at constant temperature) as its carbon content is reduced. In this figure, the original composition of the embryo is represented by  $C$  and the size of the region by  $r$ . At

temperature  $T_2$ , this region is subcritical so that stable growth cannot occur. When the carbon content has been reduced to  $C_1$ , the critical size corresponds to that of the embryo and stable growth becomes possible. It is suggested that the reduction of carbon content required for activation of the embryo is accomplished by precipitation of carbide particles within the ferrite. Since the bainite plate must advance into austenite of average carbon content, its growth rate is controlled by diffusion of carbon from the surrounding austenite to the carbide particles precipitated within the ferritic phase.

As illustrated in Fig. 20, the critical size for a given carbon content increases as the transformation temperature is raised. If  $r$  represents the largest embryo retained from the austenitizing treatment, bainite will not form at temperature  $T_3$ . The  $B_s$  temperature thus represents that temperature above which the largest embryo retained from the austenitizing treatment is smaller than the critical size for carbon free ferrite.

The course of the B-T curve can also be visualized in terms of this model. At a given reaction temperature ( $T_2$  in Fig. 20 for example) only those embryos will be activated which are larger than the critical size for carbon free ferrite. This would include embryos in the size range  $r$  to  $r_1$ . Once these have been activated, nucleation would stop. The transformation product associated with all of the activated embryos provides the rapid, incomplete reaction

at temperature  $T_2$ . At a lower reaction temperature,  $T_1$ , the minimum embryo size capable of activation decreases to  $r_2$ . Activation of these smaller nuclei increases the extent of decomposition which is in qualitative agreement with experimental observations.

#### The Retarded Reaction

Qualitatively, the ability of partial transformation at one temperature to retard transformation at a lower temperature is also consistent with the embryo size-concentration model of the reaction mechanism. When some transformation takes place at a high temperature in the bainite range before transformation at a lower temperature, the embryo distribution upon quenching to the lower temperature is different from that which exists after a direct quench. Transformation at the higher temperature has removed the larger embryos retained from the austenitizing temperature; however, others have been prepared for activation by precipitation of the carbide phase. In the early stages of reaction at  $T_h$ , this preparation process plays the controlling role. When the specimen is quenched to a lower temperature, the transformation initiated at  $T_h$  is arrested, and further transformation at  $T_r$  will require a new induction period. To be sure, this induction period actually is somewhat shorter than it would have been in the absence of the treatment at  $T_h$  because of the preparation process which occurred at  $T_h$ .

As transformation at  $T_h$  approaches the end of the rapid reaction, embryos larger than the minimum capable of activation at this temperature are rapidly consumed. Retardation of transformation at  $T_r$  therefore becomes more pronounced (see Figs. 12, 13, 15). The fact that the amount of retardation at  $T_r$  (for a constant time at  $T_h$ ) becomes less as  $T_r$  is lowered (Figs. 9 and 10) may be attributed to the decrease in critical size at  $T_r$  as this temperature is lowered.

Although this size-concentration model is able to explain the retardation behavior described above it provides no clue as to why the retardation treatment should lower the total extent of decomposition at the second reaction temperature; that is, the observed stabilization of the bainite transformation. Unless the total number of embryos activated in the stepped quenching treatment is different from the number activated during direct reaction at  $T_r$ , it would appear that prior transformation should not effect the total amount of decomposition. It therefore seems likely that some process is operative as a result of the treatment at  $T_h$  which effectively reduces the total number of embryos capable of activation at  $T_r$ . This process is undoubtedly closely allied to the process which produces stabilization of the austenite to martensite transformation.

### SUMMARY AND CONCLUSIONS

The transformation of austenite to bainite is characterized by the following features:

- (a) This transformation occurs only at temperatures below some temperature ( $B_s$ ). The actual value of this temperature is a function of the composition of the austenite.
- (b) The transformation is initiated after an induction period, proceeds rapidly for a period of time, and then comes to a halt. This reaction does not necessarily result in complete decomposition of the austenite.
- (c) The austenite not transformed by the rapid reaction may be most persistent.
- (d) The amount of austenite transformed by the rapid reaction increases as the transformation temperature is lowered. It is zero at  $B_s$ , and approaches one hundred percent at some lower temperature.
- (e) The temperature at which complete decomposition of the austenite is attained is relatively insensitive to composition and may be either above or below  $M_s$ .



Reaction at a low temperature in the bainite range may be retarded by partial transformation at a higher temperature. This retardation process can be characterized by the influence of prior transformation on the induction period at the lower temperature.

- (a) After partial reaction at a high temperature in the bainite range a new induction period precedes transformation at the lower temperature.
- (b) Short times at the holding temperature will shorten the normal induction period at the reaction temperature.
- (c) As reaction at the holding temperature approaches the end, the induction period at the lower temperature becomes longer.
- (d) This retardation at the lower temperature continues even after transformation at the holding temperature has stopped.
- (e) For a specific treatment (holding time and temperature) the amount of retardation becomes less as the reaction temperature is lowered.
- (f) At a fixed reaction temperature, greater retardation is associated with lower values of the holding temperature.

The retardation phenomenon observed in these stepped quenching experiments is revealed in the end-quenched test as an appreciable increase in hardenability. This increase can be achieved with only a slight sacrifice in maximum hardness of the heat treated steel.

Partial transformation at a high temperature in the bainite range does not eliminate the characteristic inability of the bainite reaction to consume all the austenite. In fact, the extent of austenite decomposition at the lower temperature can be reduced from its normal value by the high temperature treatment. This suggests that a stabilization process similar to that observed in the austenite-martensite reaction is also operative in the bainite range. The completion ( $B_f$ ) temperature is essentially unaffected by the prior transformation.

BIBLIOGRAPHY

1. F. Wever and others: A series of papers in Mitt. K.W.I. Eisenforschung 1930 to 1940. Summarized by F. Wever: On Transformation Kinetics. Stahl und Eisen (1949) 69, p. 664.
2. E. S. Davenport and E. C. Bain: Transformation of Austenite at Constant Subcritical Temperatures. Trans. AIME (1930), 90, p. 117.
3. F. Wever and H. Lange: On Transformation Kinetics I. Mitt. K.W.I. Eisenforschung (1932), 14, p. 71.
4. W. T. Griffiths, L. B. Pfeil and N. P. Allen: The Intermediate Transformation in Alloy Steels. Second Report, Alloy Steels Research Committee, Iron and Steel Institute. (1939), p. 343.
5. R. A. Flinn, E. Cook and J. A. Fellows: Quantitative Study of Austenite Transformation. Trans. ASM (1943), 31, p. 41.
6. T. Lyman and A. R. Troiano: Influence of Carbon Content Upon the Transformation in 3 Percent Chromium Steels. Trans. ASM (1946), 37, p. 402.
7. T. Lyman and A. R. Troiano: Isothermal Transformation of Austenite in One Percent Carbon, High-Chromium Steels. Trans. AIME (1945), 162, p. 196.
8. E. P. Klier and T. Lyman: The Bainite Reaction in Hypoeutectoid Steels. Trans. AIME (1944), 158, p. 394.
9. H. Lange and K. Mathieu: On the Progress of Austenite Decomposition in the Supercooled State in Iron-Nickel-Carbon Alloys. Mitt. K.W.I. Eisenforschung. (1938), 20, p. 125.
10. F. Wever and K. Mathieu: On the Transformations in Manganese Steels. Mitt. K.W.I. Eisenforschung. (1940), 22, p. 9.
11. J. P. Sheehan, C. A. Julien and A. R. Troiano: The Transformation Characteristics of Ten Selected Nickel Steels. Trans. ASM (1949), 41, p. 1165.
12. A. Gulyaev: Decomposition of Austenite in High-Speed Steel at Constant Temperature. Metallurg (1940), 15, (9), p. 43.

13. S. Steinberg and V. Zyuzin: The Transformation of Austenite In High-Speed Steel. Arch. Eisenhüttenwesen (1934), 7, p. 537.
14. S. Steinberg and V. Zyuzin: Study of the Transformation of Austenite in a Chromium Steel. Rev. de Metal. (1934), 31, p. 554.
15. P. Gordon, M. Cohen and R. S. Rose: Kinetics of Austenite Decomposition in High-Speed Steel. Trans. ASM (1943), 31, p. 161.
16. R. T. Howard, and M. Cohen: Austenite Transformation Above and Within the Martensite Range. Trans. AIME (1949), 176, p. 384.
17. A. R. Troiano: The Transformation and Retention of Austenite In SAE 5140, 2340, and T 1340 Steels of Comparable Hardenability. Trans. ASM (1949), 41, p. 1093.
18. J. Collins: M. S. Thesis. Univ. of Notre Dame (1948).
19. F. Wever and W. Jellinghaus: Resistance Measurements of the Transformation Kinetics of Austenite. Mitt. K.W.I. Eisenforschung. (1935), 15, p. 167.
20. F. B. Rote, W. C. Truckenmiller and W. P. Wood: Electrical Resistance Method for the Determination of Isothermal Transformation. Trans. ASM (1942), 30, p. 1359.
21. N. P. Allen, L. B. Pfeil and W. T. Griffiths: The Determination of the Transformation Characteristics of Alloy Steels. Second Alloy Steels Report, Iron and Steel Institute. (1939), p. 369.
22. J. H. Hollomon, L. D. Jaffe and M. R. Norton: Anisothermal Decomposition of Austenite. Trans. AIME (1946), 167, p. 419.
23. L. D. Jaffe: Anisothermal Formation of Bainite and Proeutectoid Constituents in Steels. Trans. AIME (1948), 176, p. 363.
24. A. R. Troiano: Discussion to Reference 59.
25. G. K. Manning and C. H. Lorig: Relationship Between Transformation at Constant Temperature and Transformation During Cooling. Trans. AIME, (1946), 167, p. 442.
26. W. Jellinghaus: Stimulation of the Bainite Transformation in Steels by Small Amounts of  $\alpha$ -Iron. Arch. Eisenhüttenwesen (1952), 12, p. 459.

27. T. Ko and S. A. Cottrell: The Formation of Bainite. Journ. of the Iron and Steel Institute (1952), 172, p. 307.
28. A. B. Greninger and A. R. Troiano: Crystallography of Austenite Decomposition. Trans. AIME, (1940), 140, p. 307.
29. E. P. Klier and A. R. Troiano: Ar'' in Chromium Steels. Trans. AIME (1945), 162, p. 175.
30. H. J. Elmendorf: The Effect of Varying Amounts of Martensite Upon the Isothermal Transformation of Austenite Remaining After Controlled Quenching. Trans. ASM (1944), 33, p. 236.
31. M. Cohen: Retained Austenite. Trans. ASM (1949), 41, p. 35.
32. E. R. Morgan and T. Ko: Thermal Stabilization of Austenite in Iron-Carbon-Nickel Alloys. Acta Met. (1953), 1, p. 36.
33. A. H. Cottrell: Tensile Properties of Unstable Austenite and its Low Temperature Decomposition Products. Journ. Iron and Steel Institute. (1945), 151, p. 93.
34. M. D. Jepson and F. C. Thompson: The Acceleration of the Rate of Isothermal Transformation of Austenite. Journ. Iron and Steel Institute (1949), 162, p. 49.
35. K. Winterton: A Note on the Physical Properties of an Austenitic Weld-Metal and its Structural Transformations on Straining. Journ. Iron and Steel Institute. (1945), 151, p. 87.
36. G. J. Guarnieri and J. J. Kanter: Some Characteristics of the Metastable Austenite of 4 to 6% Chromium Plus 1/2% Molybdenum Cast Steel. Trans. ASM (1948), 40, p. 1147.
37. R. C. Hall: M. S. Thesis, Case Institute of Technology. (1952).
38. Anonymous: Isothermal Transformation Diagrams for Nickel Steels. Metallurgia (1951), May, p. 234 and June, p. 280.
39. G. Delbart and M. Ravery: Research on Isothermal Transformation of Austenite in France and Abroad. Rev. de Met. (1949), 46, p. 475.
40. A. R. Troiano and J. E. DeMoss: Transformations in Krupp-Type Carburizing Steels. Trans. ASM (1947), 39, p. 788.

41. Unpublished Research at Case Institute of Technology
42. E. Houdremont, W. Koch and H. J. Wiester: On the Process of Transformation in Chromium and Manganese Steels. Arch. Eisenhüttenwesen (1945), 18, p. 147.
43. A. Hultgren: Jernkontorets Annaler. (1951), 135, p. 403.
44. A. Hultgren: Isothermal Transformation of Austenite. Trans. ASM (1947), 39, p. 915.
45. F. Wever, A. Rose, and W. Peter: On the Transformation Behavior and Tempering Stability of Steel with Special Carbide Forming Alloying Elements, Represented in an example of a Vanadium Steel. Arch. Eisenhüttenwesen. (1950), 21, p. 367.
46. W. Crafts and J. L. Lamont: Carbides in Isothermally Transformed Chromium Steels. Trans. AIME (1949), 185, p. 957.
47. W. Koch and H. J. Wiester: New Contributions to the Knowledge of Carbides in Alloy Steels. Stahl und Eisen. (1949), 69, p. 73.
48. A. E. Austin and C. M. Schwartz: Electron-Diffraction Study of Iron Carbides in Bainite and Tempered Martensite, ASTM Preprint No. 165, (1952).
49. A. Rose and W. Peter: Stahl und Eisen. (1952), 72, p. 1063.
50. J. A. Cameron: Application of the Isothermal Transformation Diagram to the Normalizing of E.N. 40C Steel. Journ. Iron and Steel Institute. (1952), 170, p. 313.
51. L. M. Pevzner, G. M. Rovenski and T. D. Kubyshkina: Redistribution of Carbon During Transformation in Bainite Range. Dok. Akad. Nauk SSSR (1952), 85, p. 811.
52. V. Gridnev and G. Kurdjumov: Teoriya i Praktika Metallurgii. (1936), 8, p. 2.
53. A. B. Greninger and A. R. Troiano: The Martensite Transformation. Metals Handbook, ASM (1948), p. 263.
54. W. J. Harris, Jr. and M. Cohen: Stabilization of the Austenite-Martensite Transformation. Trans. AIME (1949), 180, p. 447.

55. R. F. Mehl: Decomposition of Austenite by Nucleation and Growth Processes, Journ. Iron and Steel Institute (1948), 159, p. 113.
56. H. J. Wiester: Structure of the Intermediate Range in Steel and Its Origin. Arch. Eisenhüttenwesen (1944), 18, p. 97.
57. E. S. Davenport: Isothermal Transformation in Steels. Trans. ASM (1939), 27, p. 837.
58. G. V. Smith and R. F. Mehl: Lattice Relationships in Decomposition of Austenite to Pearlite, Bainite and Martensite. Trans. AIME (1942), 150, p. 211.
59. C. Zener: Kinetics of the Decomposition of Austenite. Trans. AIME (1946), 167, p. 550.
60. J. C. Fisher: Eutectoid Decompositions. Thermodynamics in Physical Metallurgy. ASM (1950), p. 201.
61. A. Schrader and F. Wever: On the Question of the Adaptation of the Electron Microscope For the Structural Investigation of Steels. Arch. Eisenhüttenwesen (1952), 23, p. 489.
62. R. F. Mehl: Physics of Hardenability. Hardenability of Alloy Steels. ASM (1939), p. 1.
63. J. R. Vilella, G. E. Guellich and E. C. Bain: On Naming the Aggregate Constituents in Steel. Trans. ASM (1936), 24, p. 225.
64. F. Wever: Concerning the Transformations in the Hardening of Steel. Ztsch. für Metall. (1932), 24, p. 270.
65. C. A. Beiser: B. S. Thesis, Case Institute of Technology. (1951).
66. R. A. Flinn, M. Cohen and J. Chipman: The Acicular Structure in Nickel-Molybdenum Cast Irons. Trans. ASM (1942), 30, p. 1255.
67. R. T. Howard and M. Cohen: Quantitative Metallography by Point Counting and Lineal Analysis. Trans. AIME (1947), 172, p. 413.
68. E. S. Machlin and M. Cohen: Isothermal Mode of the Martensite Transformation. Journ. of Metals (1952), 4, p. 489.

69. E. S. Davenport, R. A. Grange and R. J. Hafsten: Influence of Austenite Grain Size Upon Isothermal Transformation Behavior of SAE 4140 Steel. Trans. AIME (1941), 145, p. 301.
70. S. A. Cottrell and T. Ko: Effects of High Temperature Heating On the Isothermal Formation of Bainite. Journ. of the Iron and Steel Institute (1953), 173, p. 224.
71. Electron Microstructure of Bainite in Steel: ASTM Bulletin (1952), May, p. 62.
72. M. Avrami: Kinetics of Phase Change, I. Journ. Chem. Phys. (1939), 7, p. 1103.
73. D. P. Antia, S. Fletcher and M. Cohen: Structural Changes During the Tempering of High Carbon Steels. Trans. ASM (1944), 32, p. 290.
74. A. Hultgren: Isothermal Transformation of Austenite and Partitioning of Alloying Elements in Low Alloy Steels. Kungl. Svenska Vetenskapsakademiens Handlingar (1953), 4, p. 3.
75. C. A. Liedholm and W. C. Coons: Effect of Cooling Transformation Upon Subsequent Isothermal Transformation. Metal Progress (1946), 46, p. 104.
76. H. Jolivet and A. Portevin: The Induction Period Preceding Austenite Decomposition. Compt. Rend. (1941), 213, p. 687.
77. A. R. Troiano: Unpublished Research.
78. D. Turnbull: Kinetics of Heterogeneous Nucleation. Chem. Phys. (1950), 18, p. 198.
79. J. C. Fisher, J. H. Hollomon and D. Turnbull: N Journ. of App. Phys. (1948), 19, p. 775.



## FIGURES

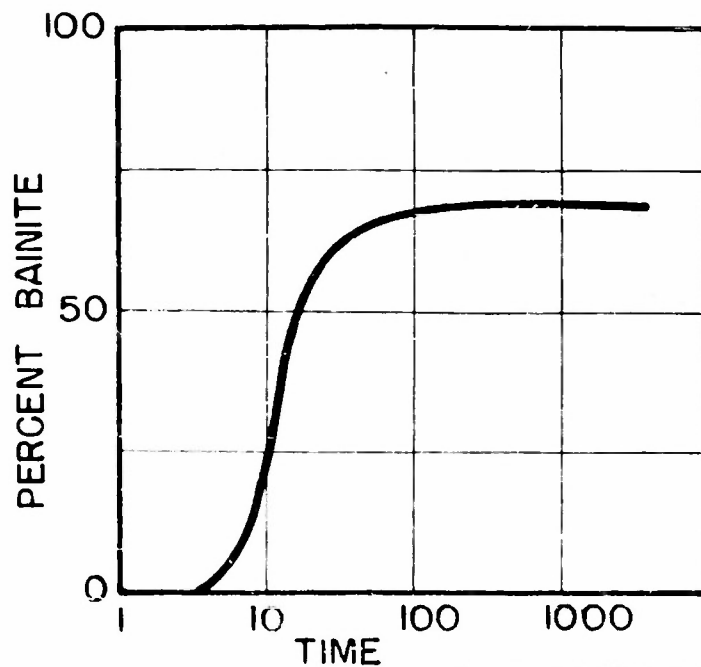


FIG.1: PROGRESS OF THE ISOTHERMAL BAINITE REACTION (SCHEMATIC)

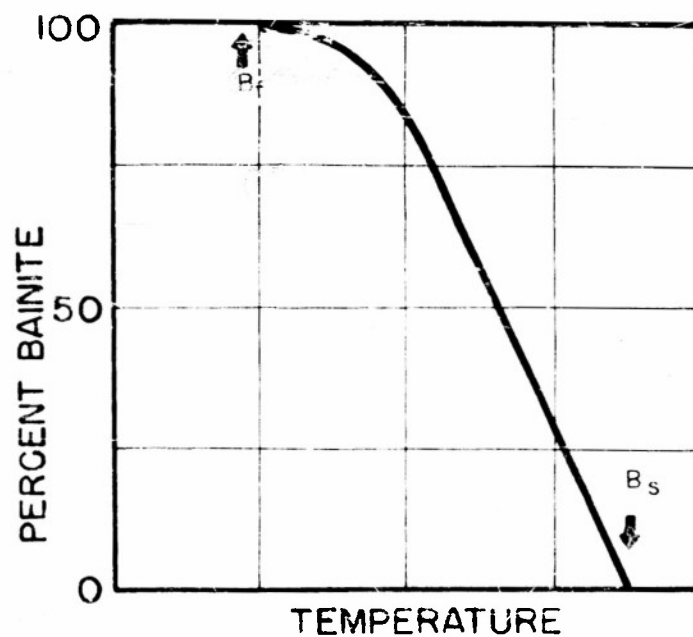


FIG.2: INFLUENCE OF REACTION TEMPERATURE ON THE AMOUNT OF BAINITE FORMED IN THE ISOTHERMAL REACTION. B-T CURVE. (SCHEMATIC).

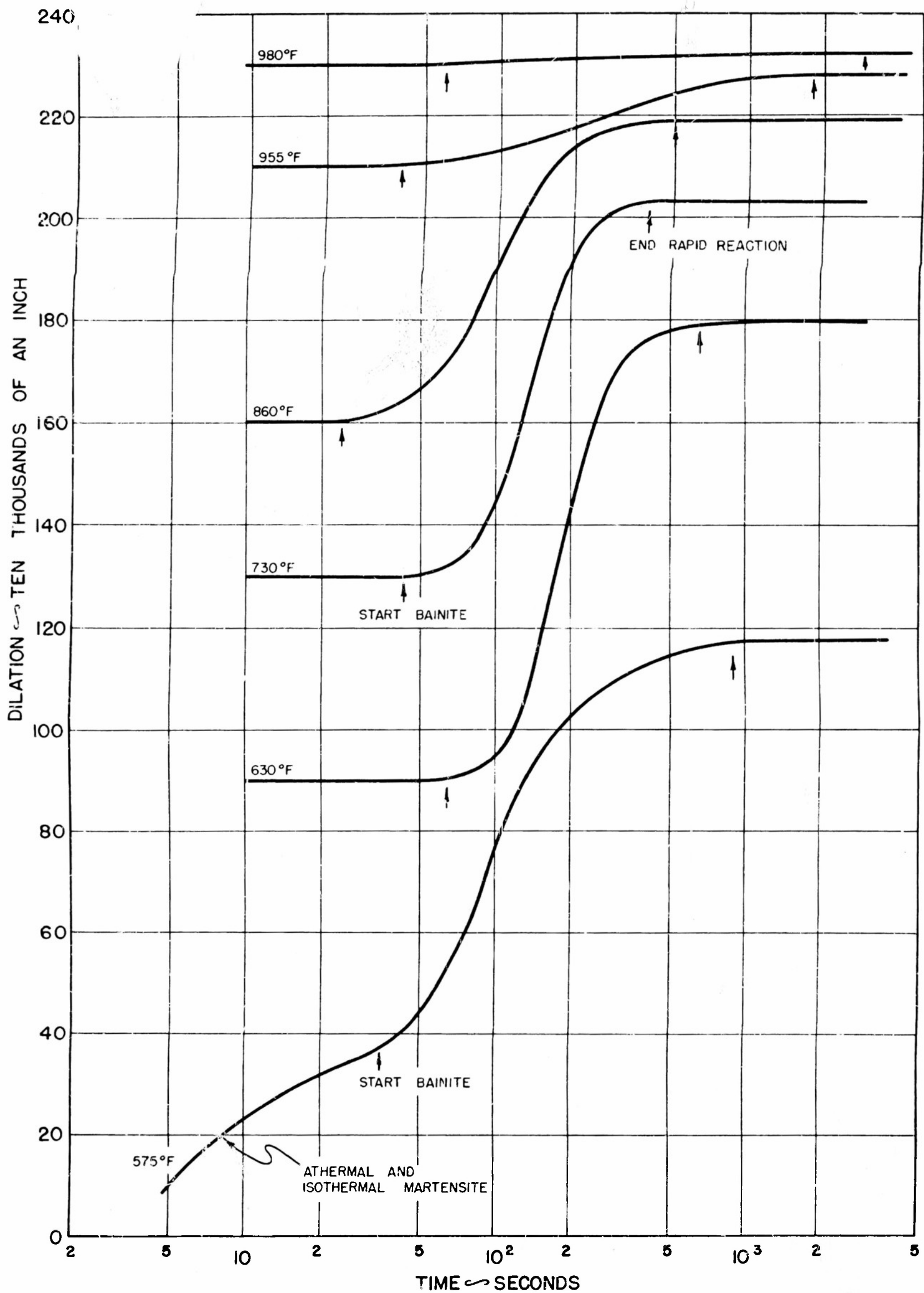


FIG. 3 : ISOTHERMAL EXPANSION CURVES FOR 4340 STEEL.

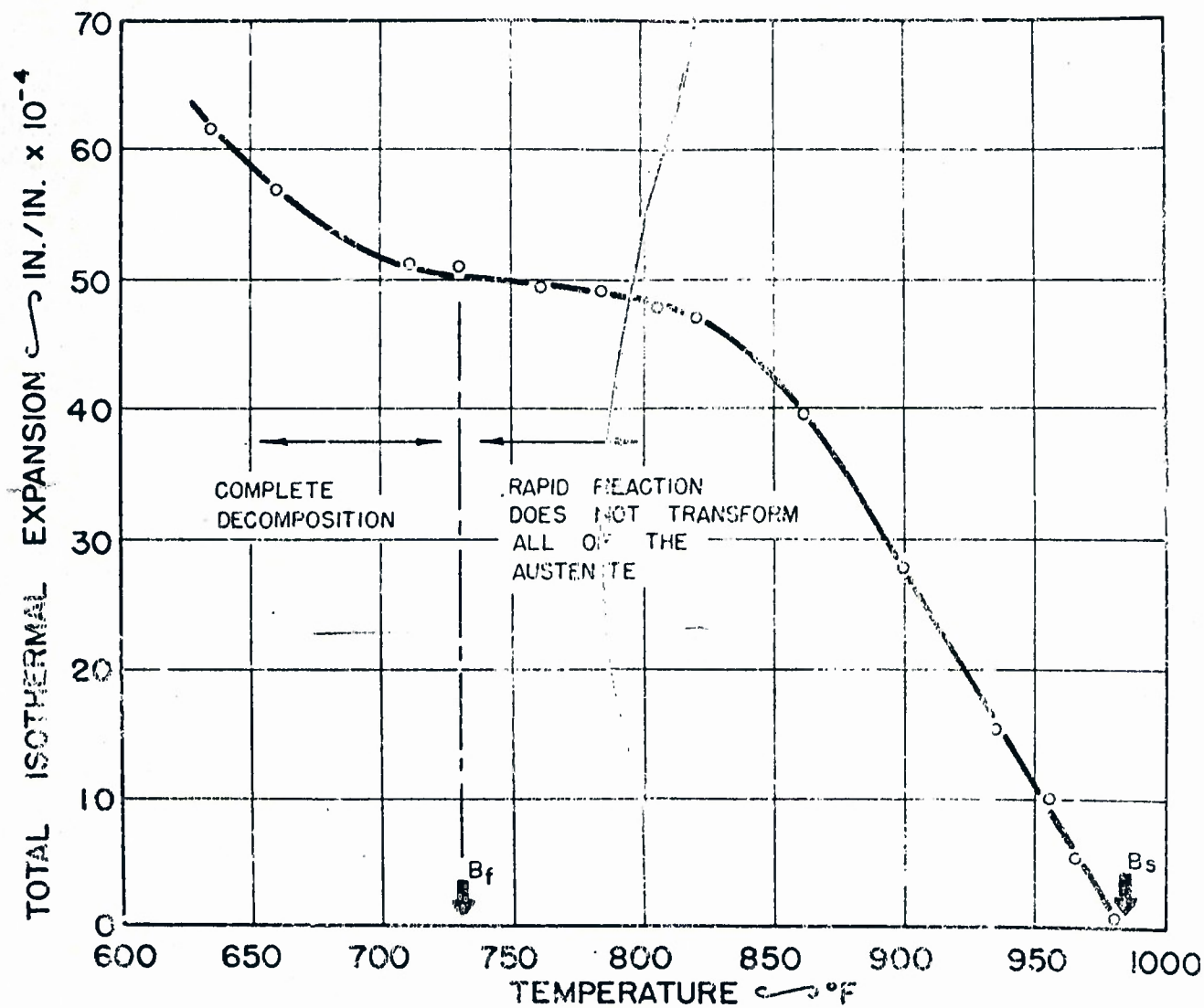


FIG. 4: TOTAL EXPANSION VS. TRANSFORMATION TEMPERATURE FOR 4340 STEEL.

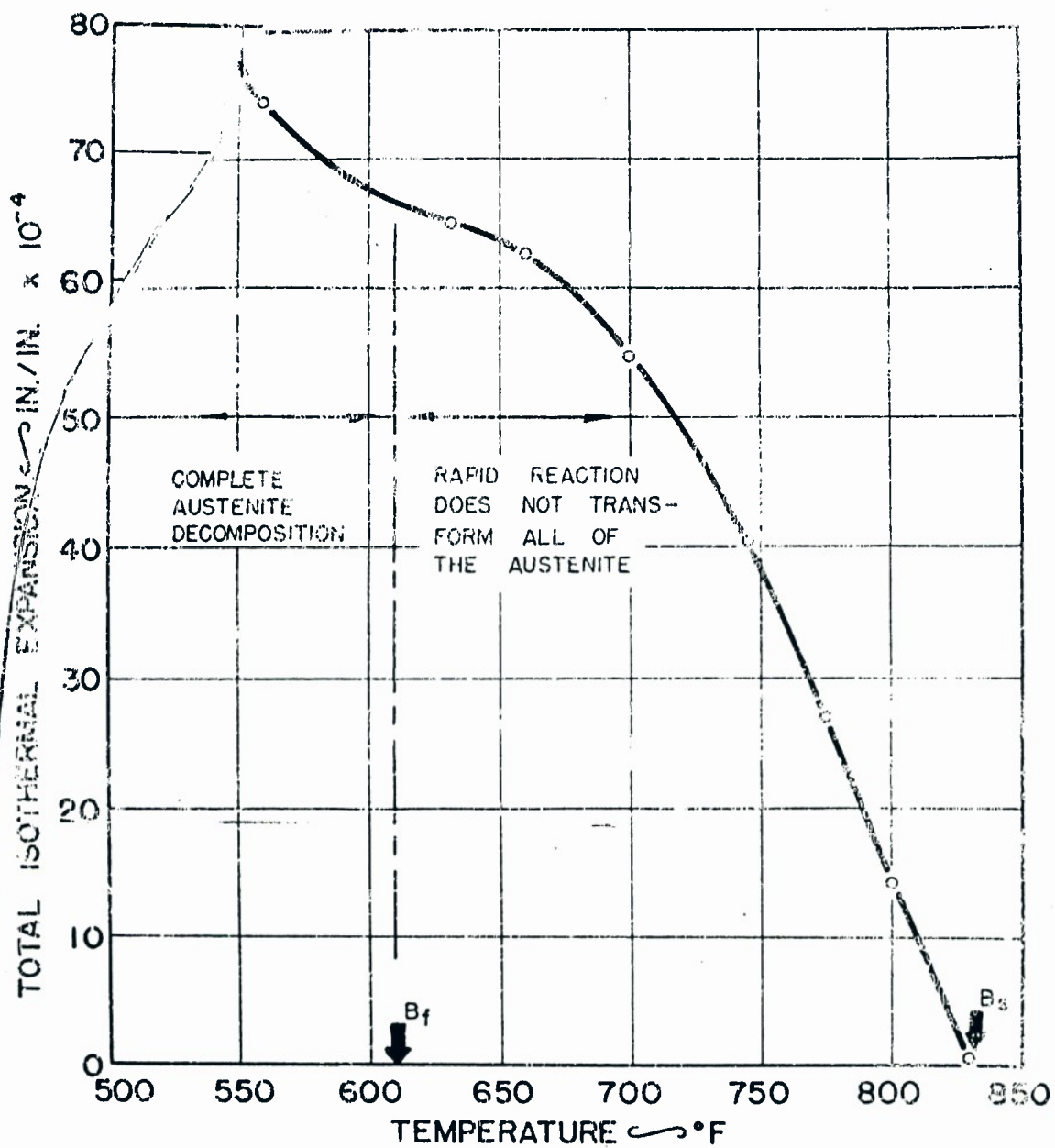


FIG. 5: TOTAL EXPANSION VS. TRANSFORMATION TEMPERATURE FOR K STEEL.

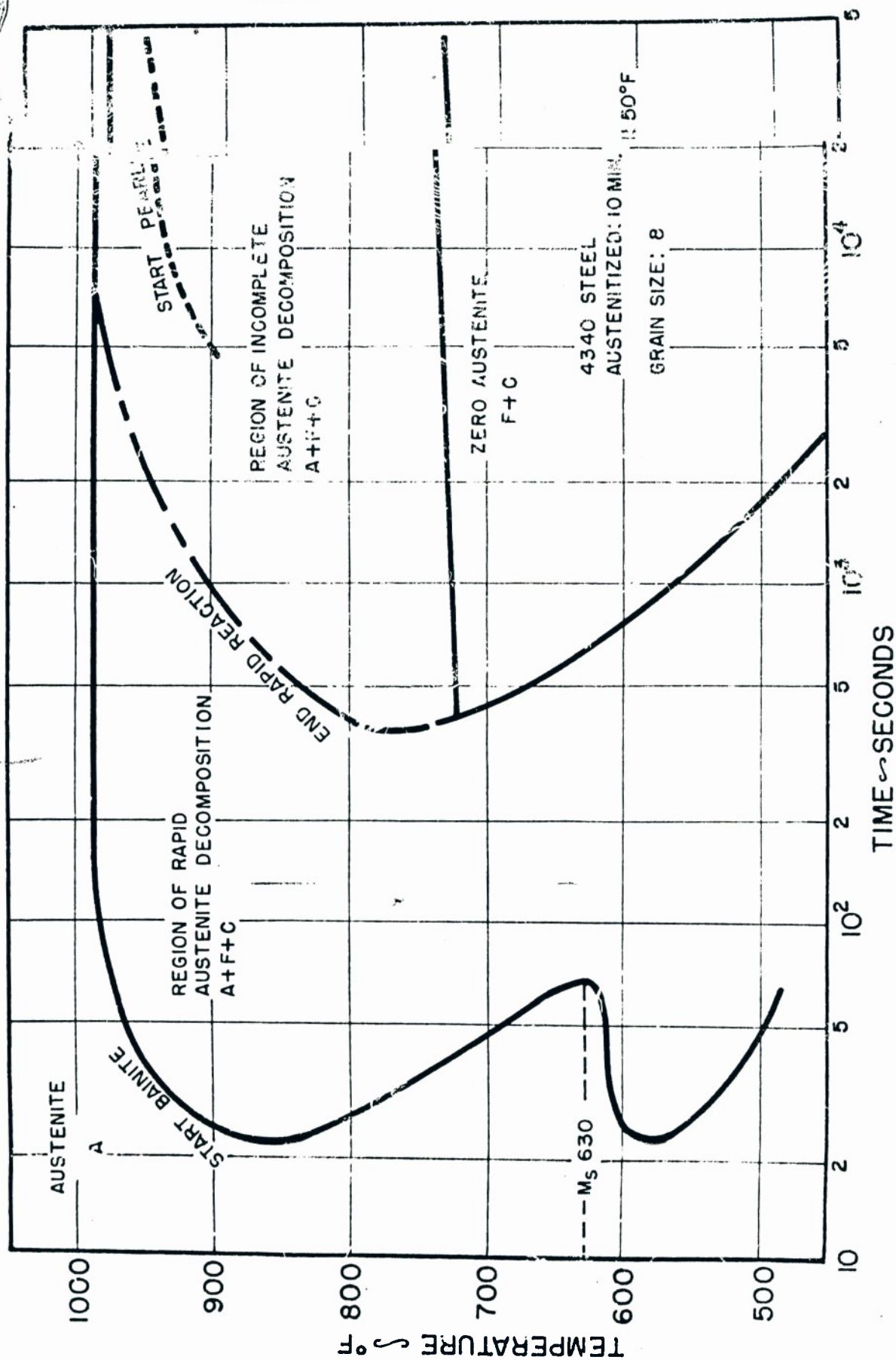


FIG. 6: ISOTHERMAL TRANSFORMATION DIAGRAM FOR BAINITE RANGE OF 4340.



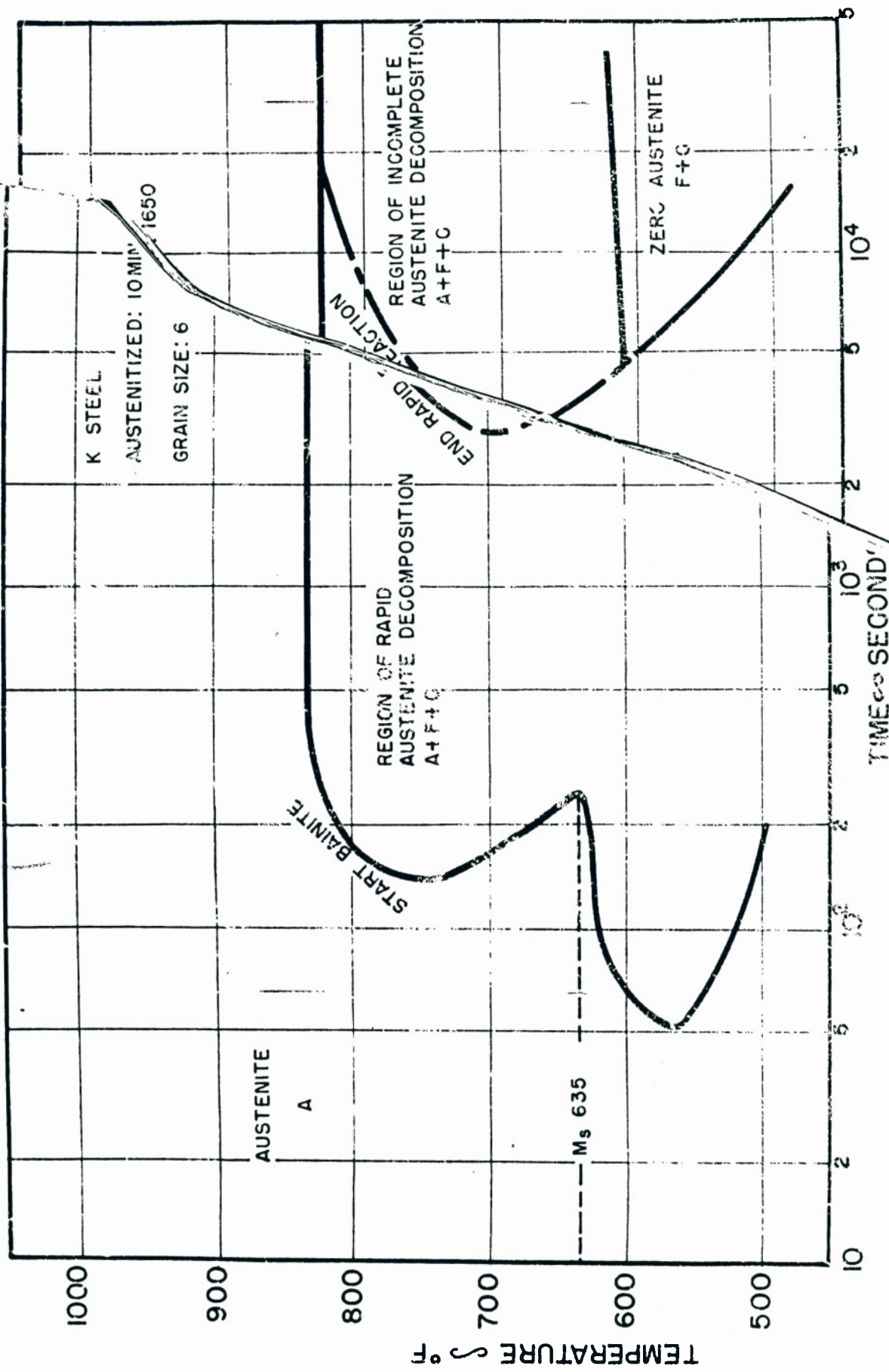


FIG. 7: ISOTHERMAL TRANSFORMATION DIAGRAM FOR BAINITE RANGE OF K STEEL

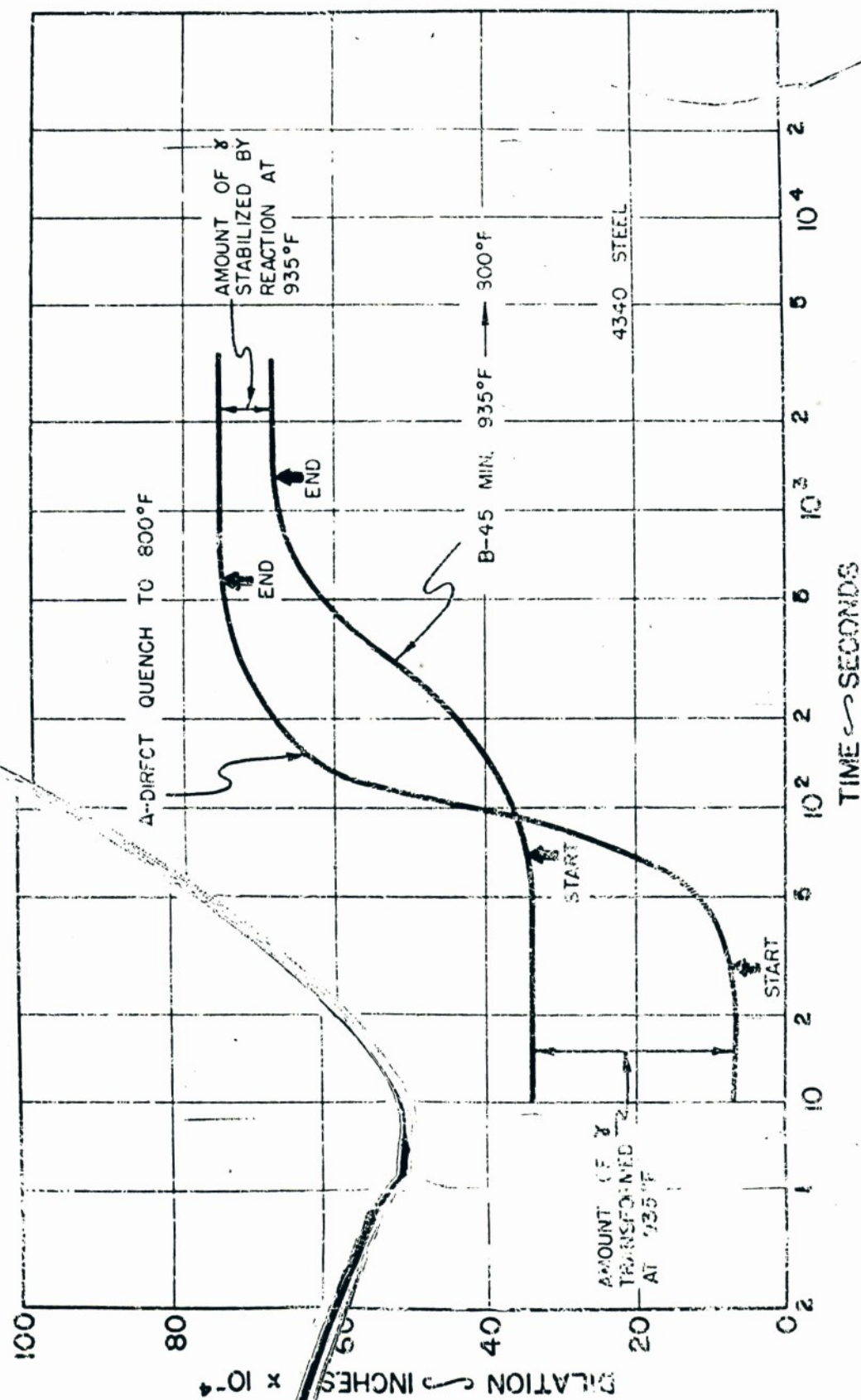


FIG. 8 : EFFECT OF PARTIAL REACTION AT 935°F ON PROGRESS OF TRANSFORMATION AT 1000°F.



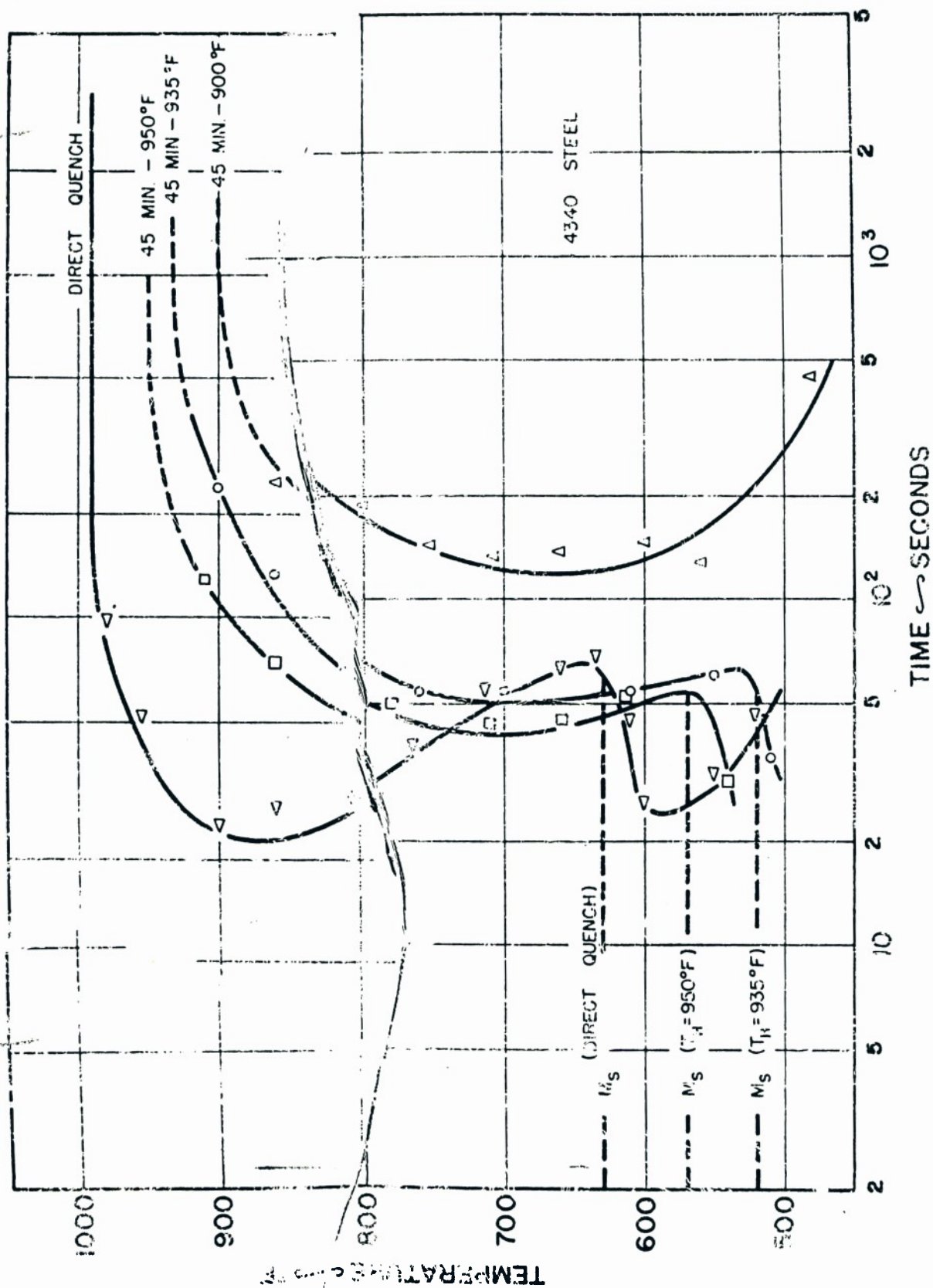


FIG. 9 : EFFECT OF 45 MINUTES AT SEVERAL TEMPS. ON INDUCTION PERIOD AT LOWER TEMPERATURES.

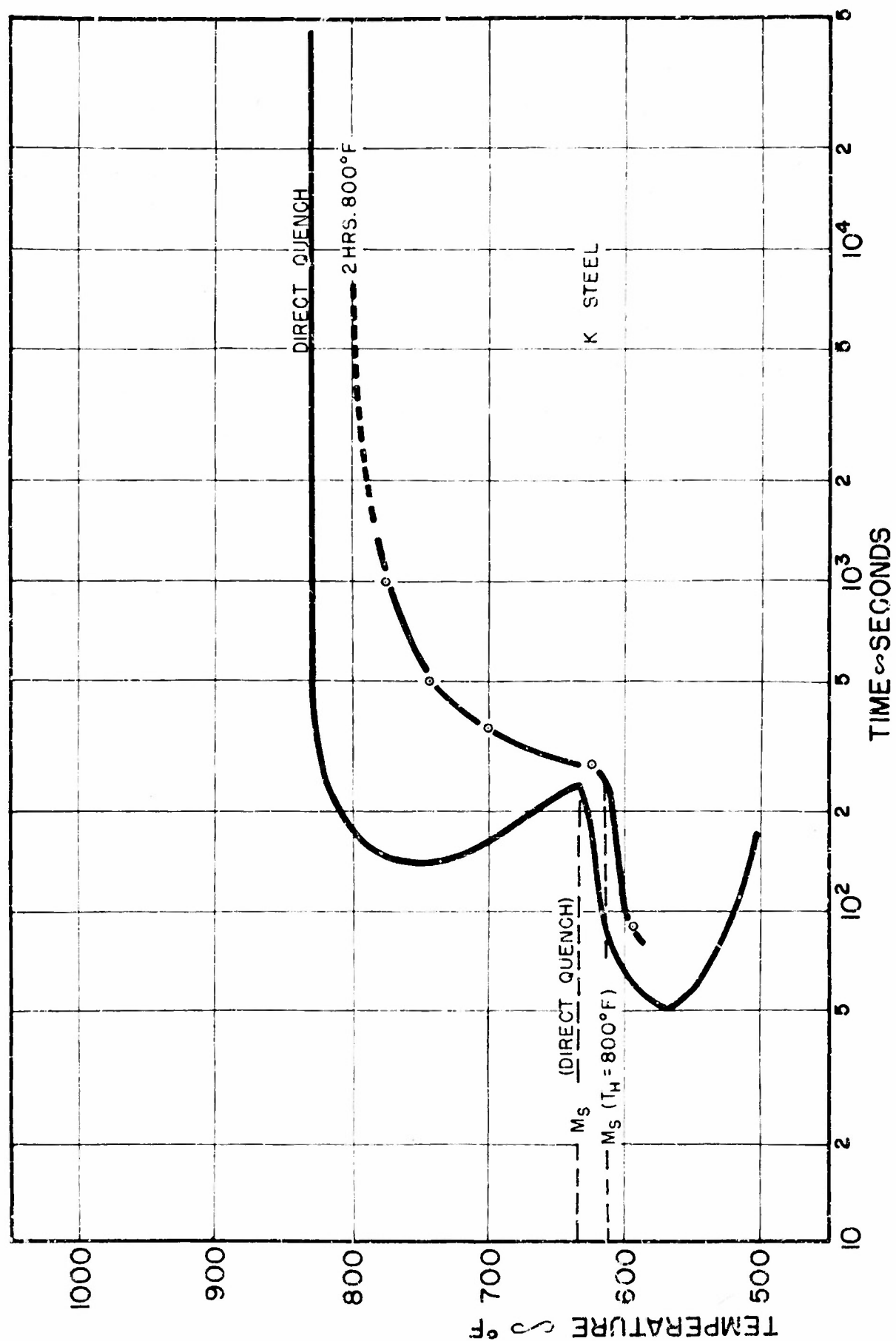


FIG. 10: EFFECT OF 2 HOURS AT 800°F ON INDUCTION PERIOD AT LOWER TEMPERATURES.

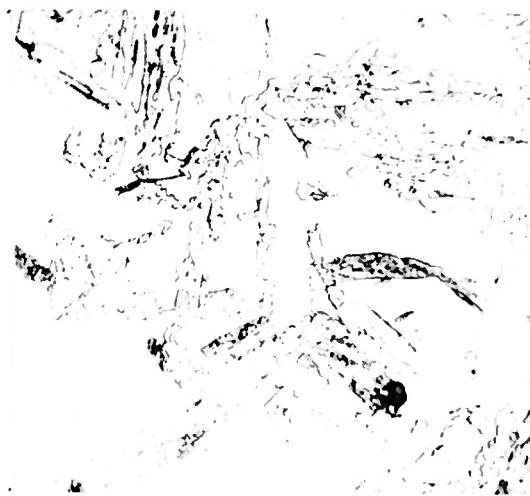
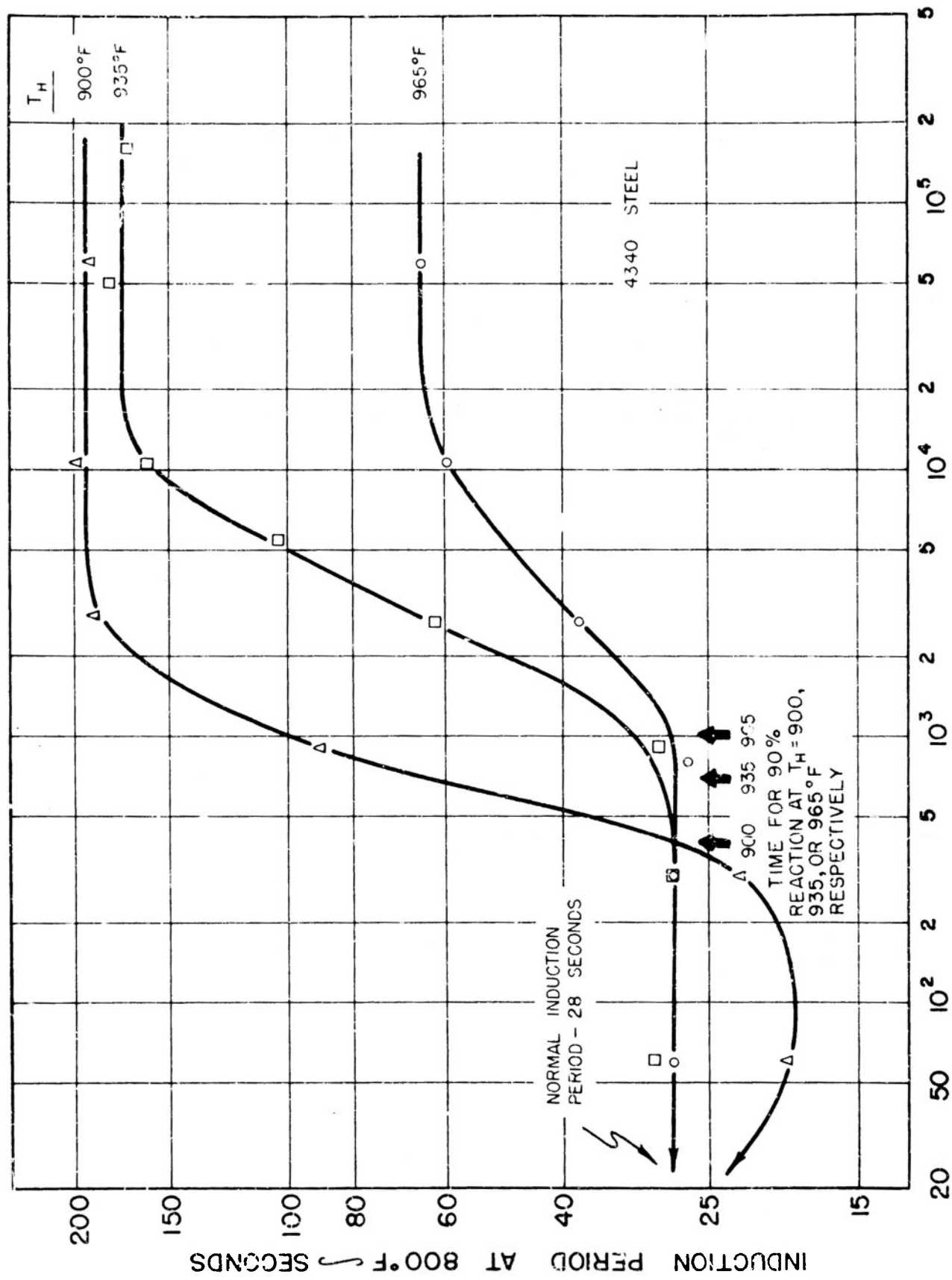


FIG. II: STRUCTURE OF 4340 PRODUCED BY REACTION FOR 1 HOUR AT 930°F FOLLOWED BY 3 MINUTES AT 700°F. NITAL ETCH. 1200 X.



TIME AT  $T_H$  SECONDS

FIG. 12 EFFECT OF TIME AT SEVERAL HOLDING TEMPS. ON INDUCTION PERIOD AT 800°F.

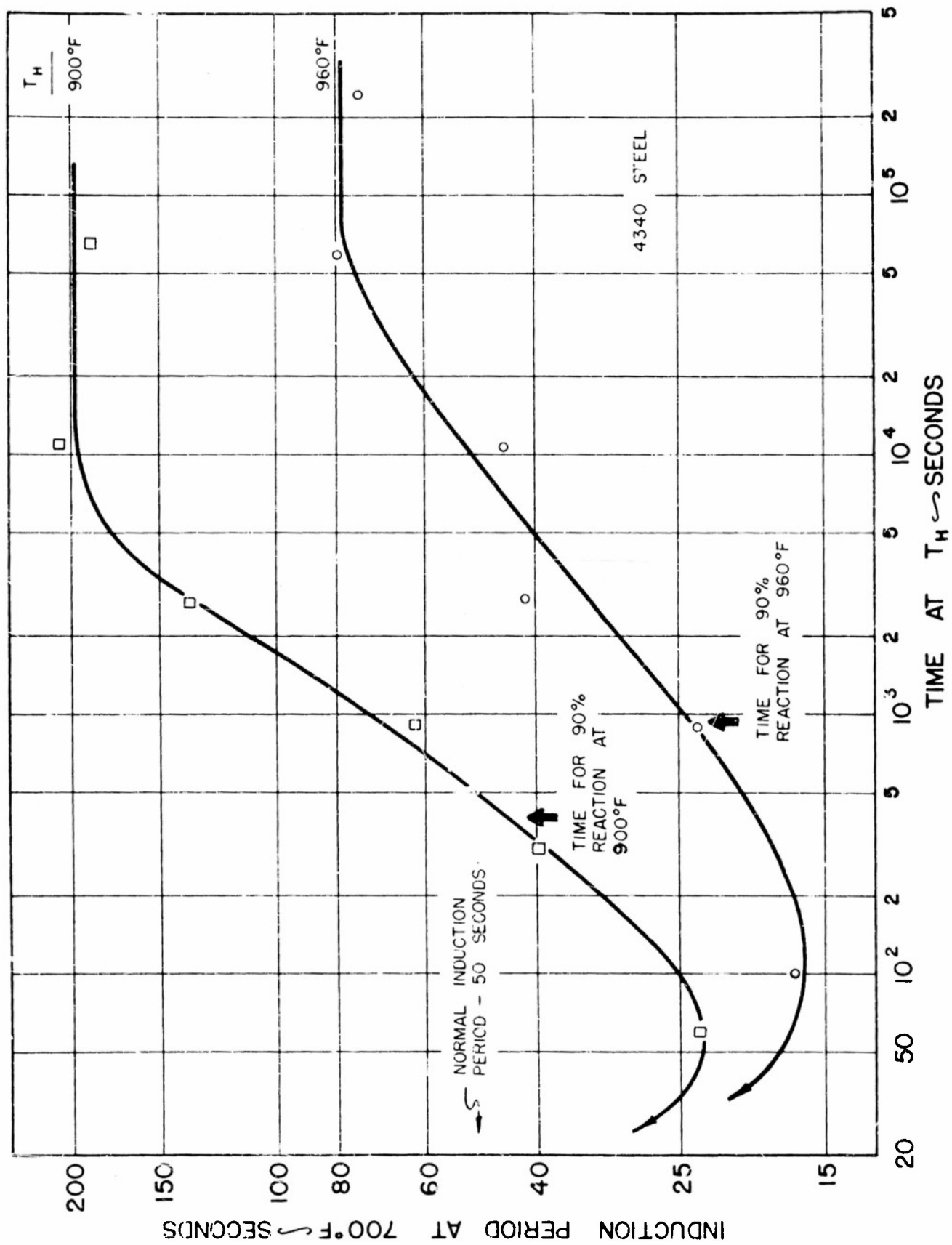


FIG.13 EFFECT OF TIME AT SEVERAL HOLDING TEMPS. ON INDUCTION PERIOD AT 700°F.



FIG. 14: STRUCTURE OF 4340 PRODUCED BY REACTION FOR 2 MINUTES AT 940°F FOLLOWED BY 50 SECONDS AT 660°F. NITAL ETCH. 800X.



FIG. 15: EFFECT OF TIME AT 800°F ON INDUCTION PERIOD AT 700°F.



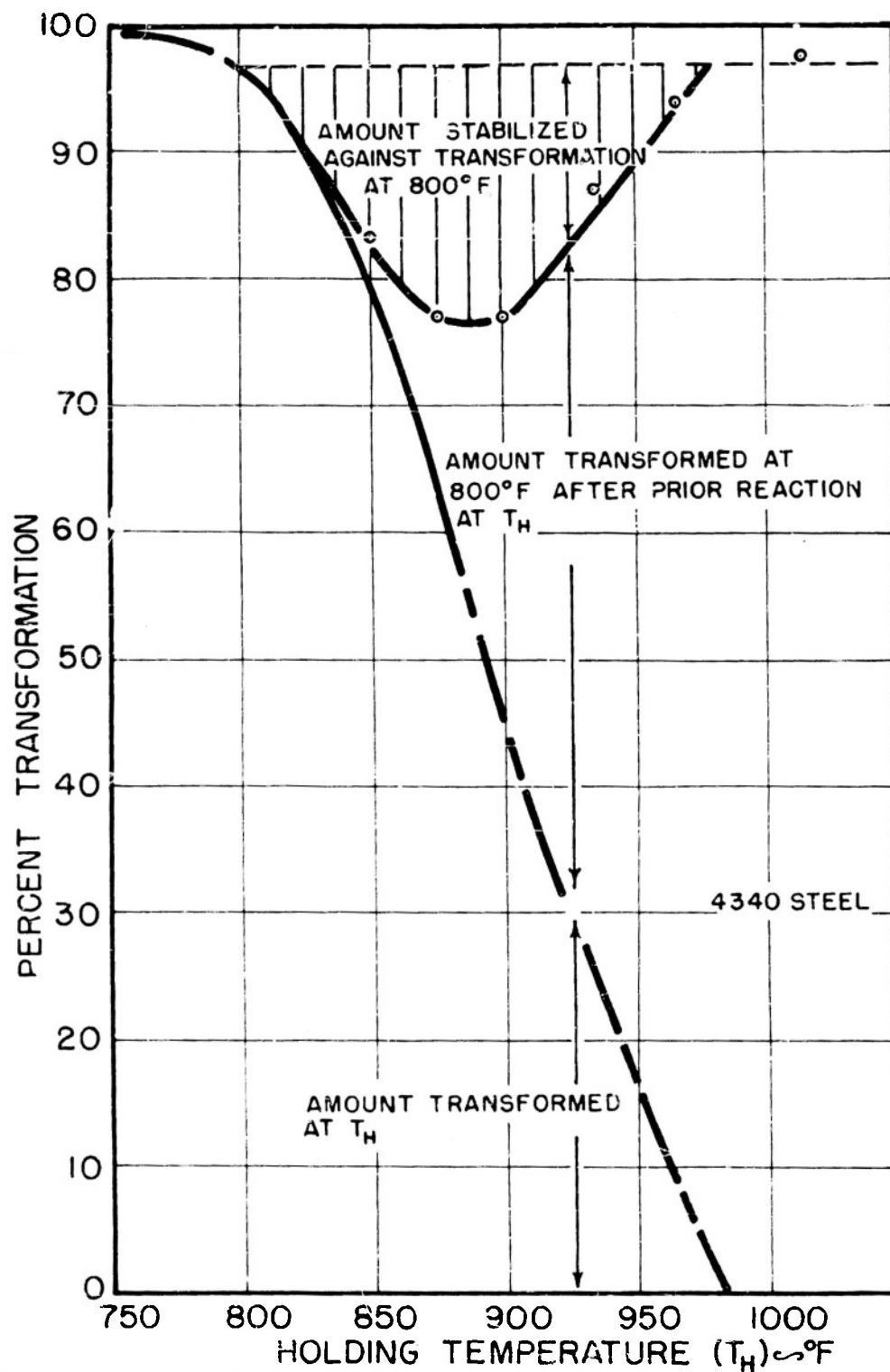


FIG.16: STABILIZATION OF AUSTENITE AT 800°F PRODUCED BY REACTION FOR 45 MIN. AT VARIOUS  $T_H$  LEVELS.



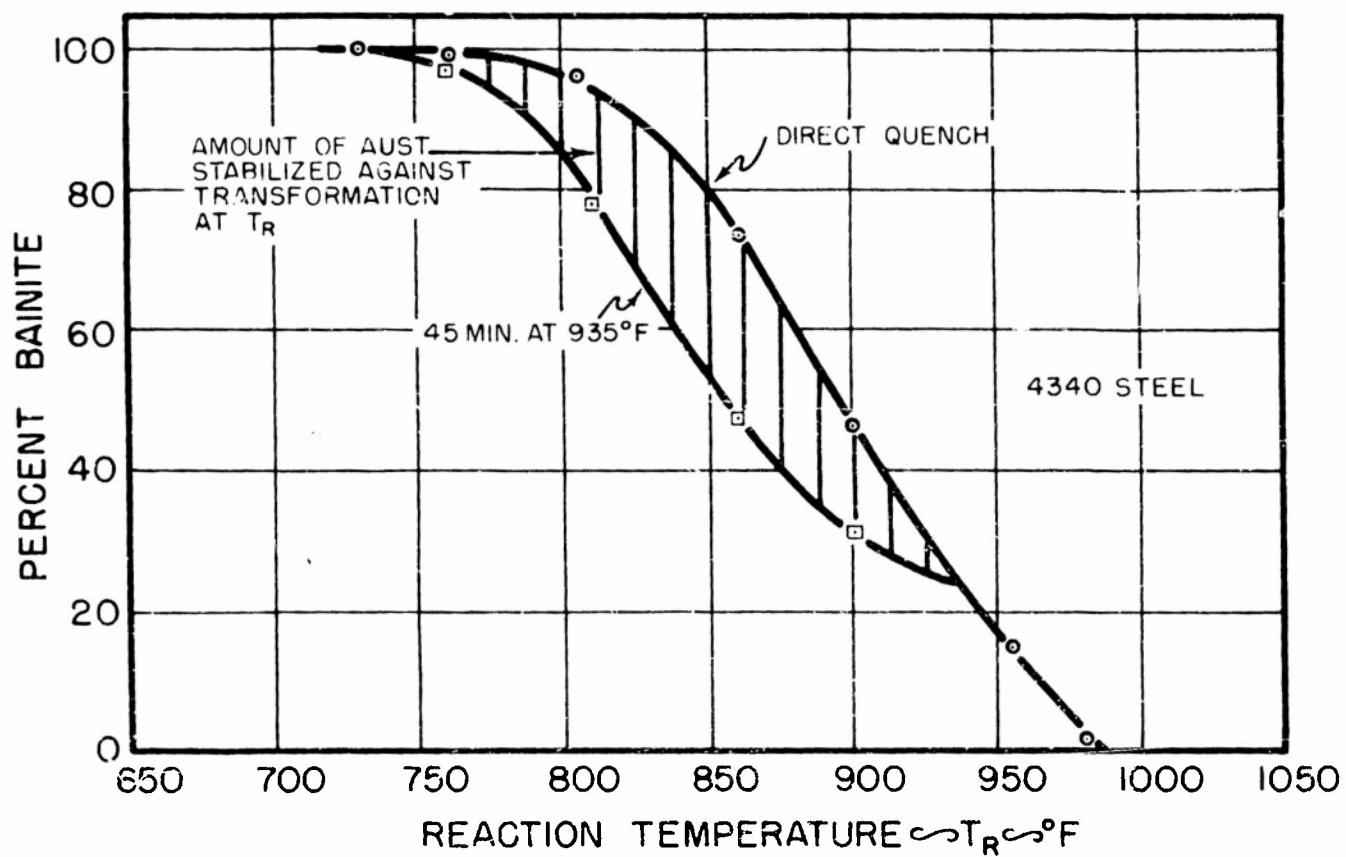


FIG 17: EFFECT OF REACTION TEMPERATURE ( $T_R$ ) ON AMOUNT OF AUSTENITE STABILIZED BY 45 MIN. AT  $T_H = 935^\circ\text{F}$ .

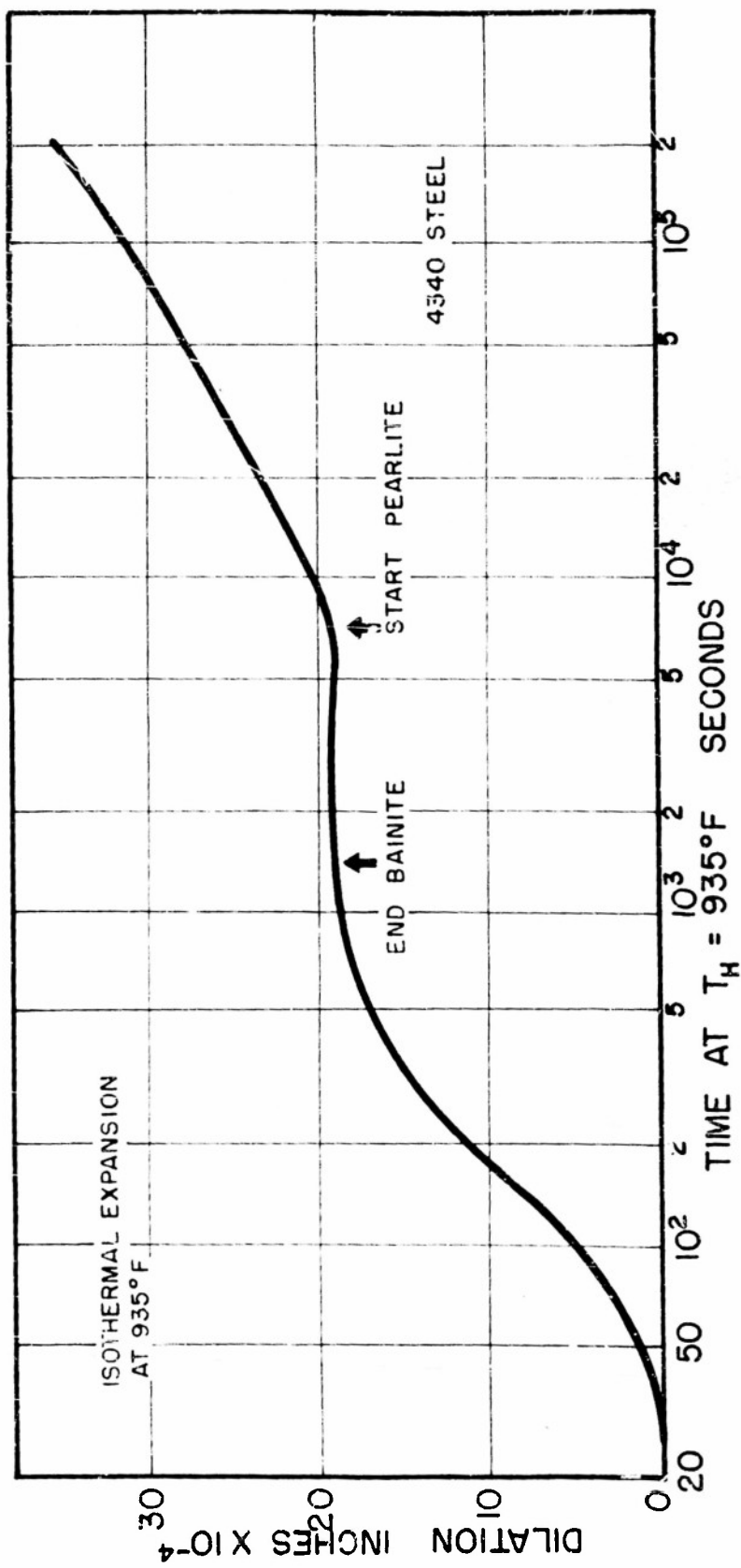
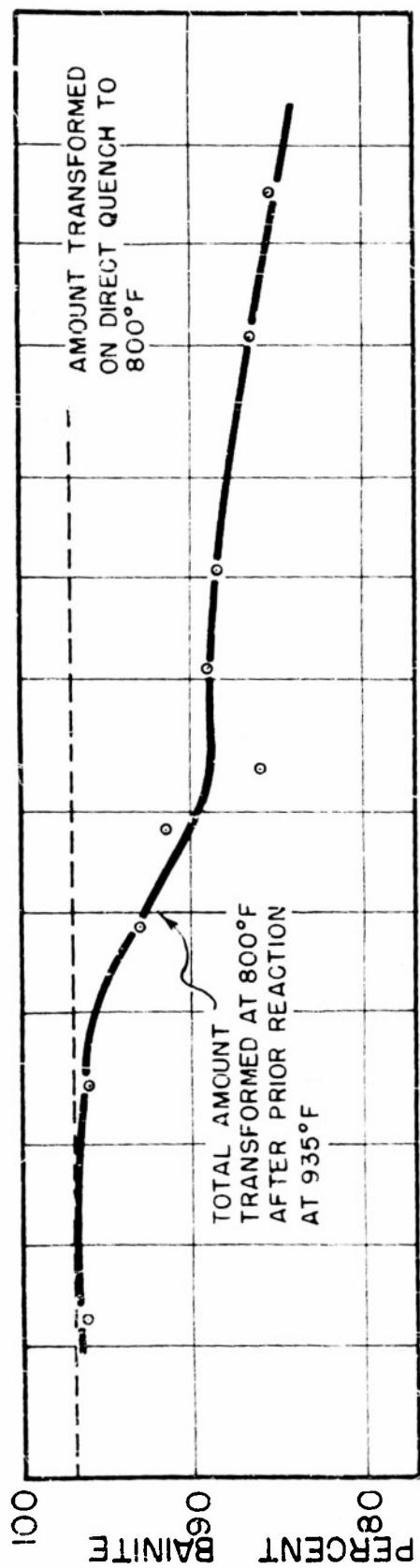
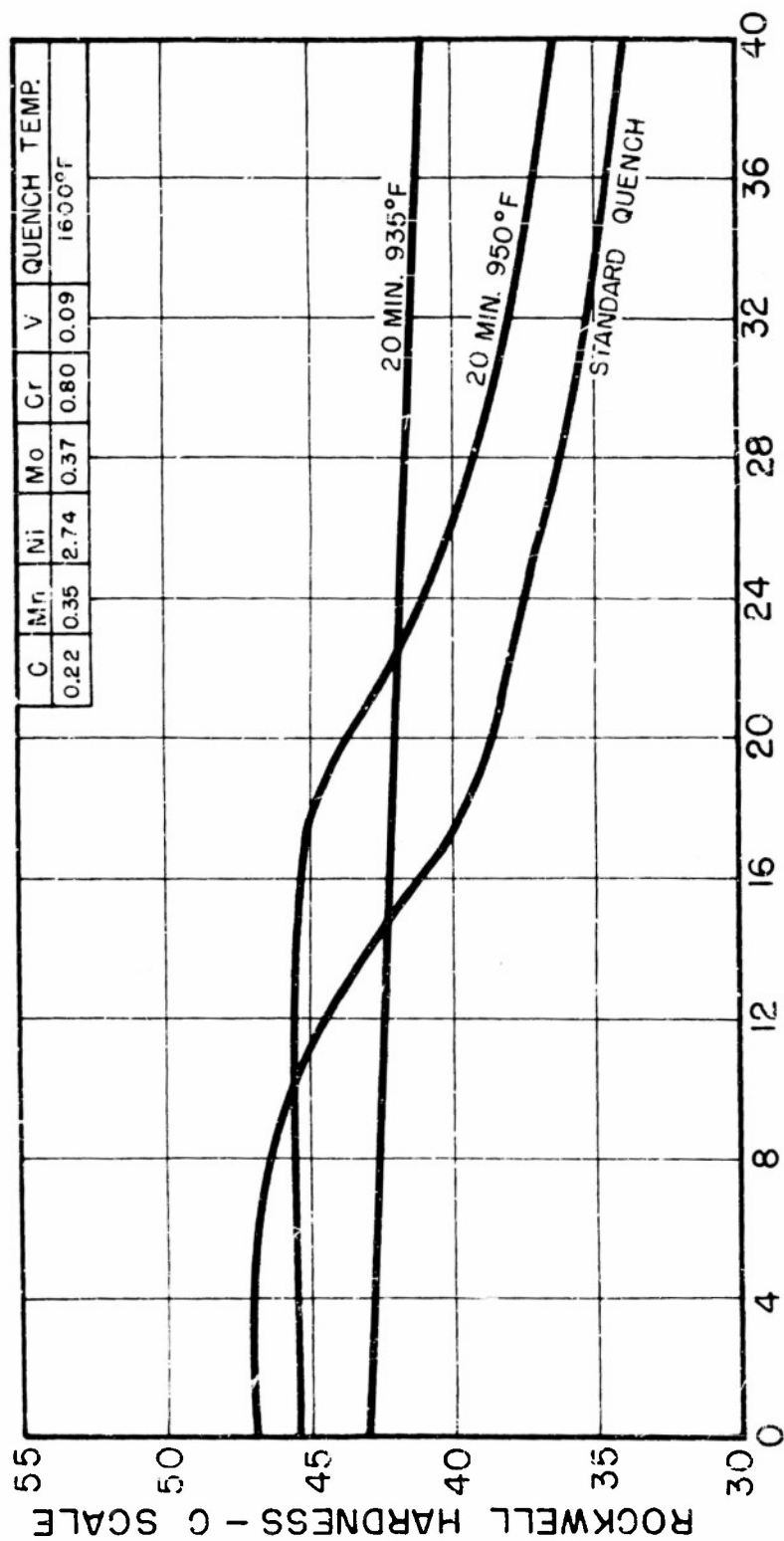


FIG.18: EFFECT OF TIME AT 935°F ON AMOUNT OF AUSTENITE TRANSFORMED AT 800°F.



DISTANCE FROM QUENCHED END ~ SIXTEENTHS OF INCH

FIG. 19: INFLUENCE OF PRIOR TRANSFORMATION ON THE END-QUENCH HARDENABILITY RESPONSE. (FROM PATENT APPLICATION DATED NOV. 1, 1947).

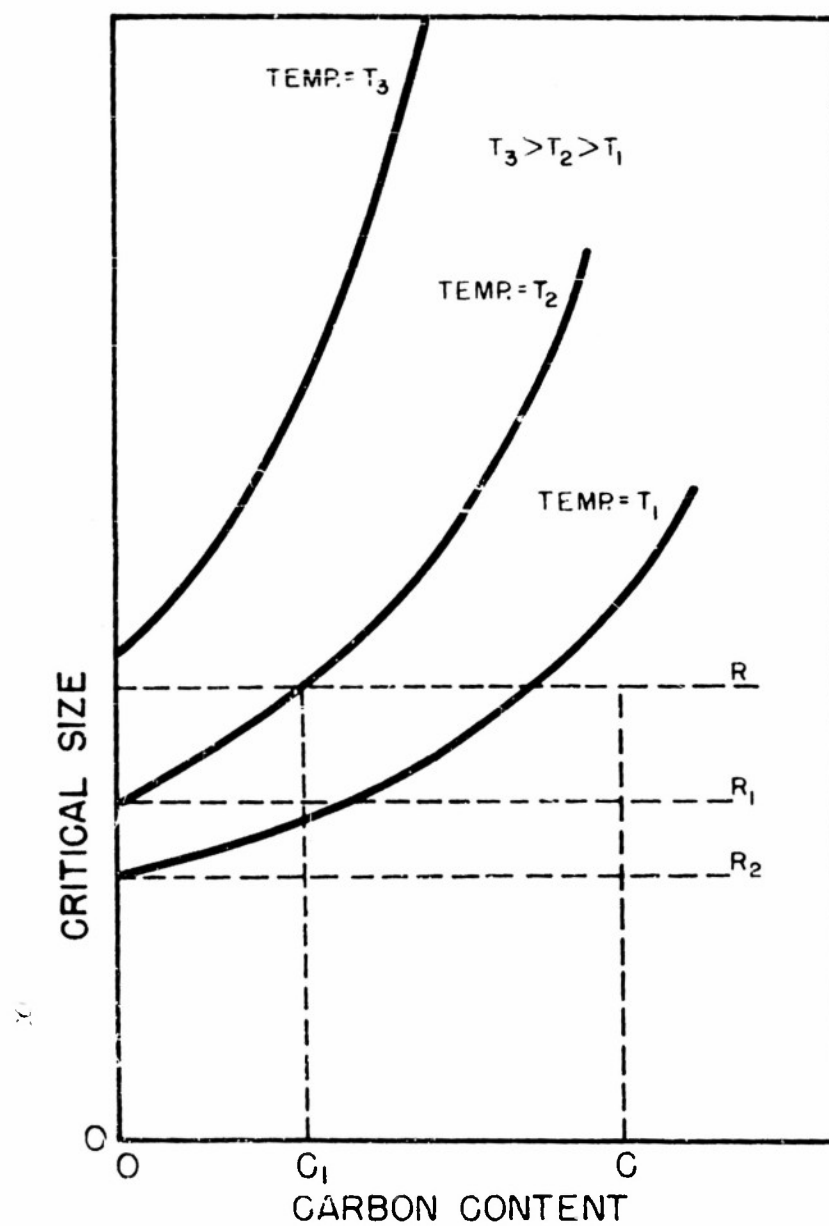


FIG. 20: SCHEMATIC ILLUSTRATION OF THE VARIATION OF CRITICAL SIZE AS A FUNCTION OF CARBON CONTENT AT SEVERAL ISOTHERMS.